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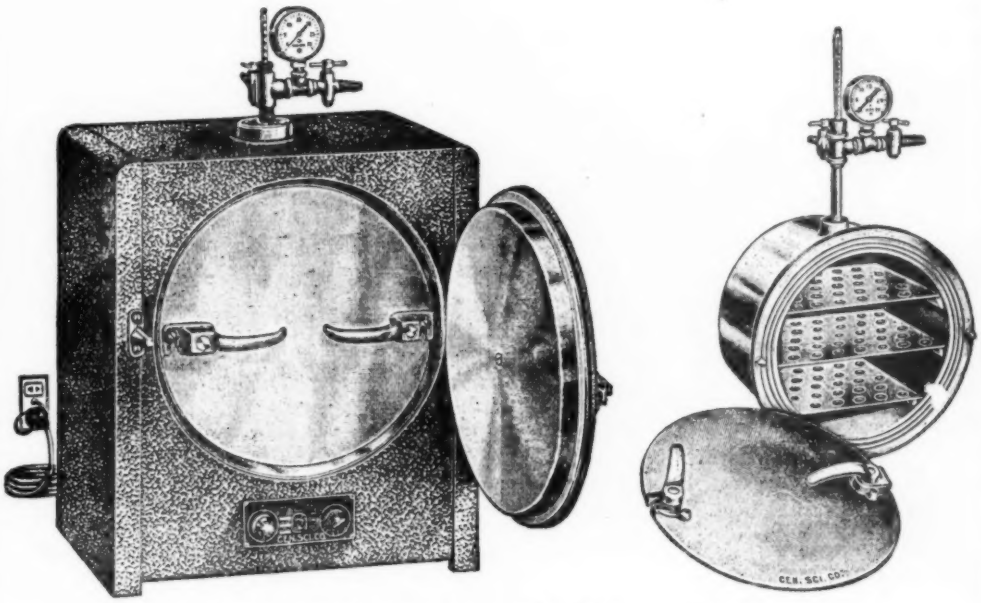

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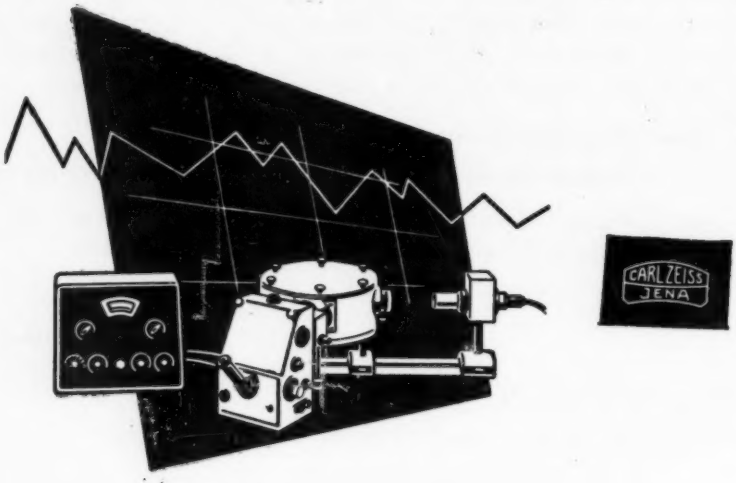

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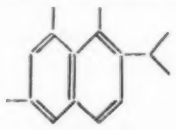
STUDIES IN SESQUITERPENES. PART XIV*. FURTHER EXPERIMENTS IN THE EUDALENE SERIES

By G. S. Krishna Rao and Sukh Dev

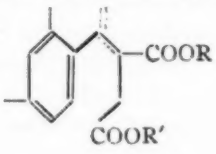
A detailed study of some of the potential intermediates in the synthesis of 3 : 8-dimethyleudalene has been made. No rearrangement during the PPA cyclisation of γ-(2 : 4-dimethylphenyl)-valeric acid to 4 : 6 : 7-trimethyltetralone-1, as claimed by Mosby (*J. Amer. Chem. Soc.*, 1952, **74**, 2564), could be detected.

In an extension of our previous work (this *Journal*, 1956, **33**, 561), it was planned to effect a synthesis of 3 : 8-dimethyleudalene (I). Two projected routes to this compound have so far been investigated ; though the planned reactions could not be pushed to a successful end, enough interesting data have accumulated during this investigation, which form the subject matter of this communication.

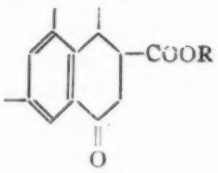
Stobbe Condensation of Diethyl Succinate and 2 : 4-Dimethylacetophenone.—In the first route, it was planned to make use of the half-ester (IIa) resulting from the condensation of diethyl succinate and 2 : 4-dimethylacetophenone. It was anticipated that its reduction would yield the dihydro derivative, from which the keto-ester (III) could be obtained ; the conversion of the carbethoxy group of its desoxy derivative into an *iso*propyl moiety was expected to give rise to a compound suitable for dehydrogenation to (I). However, since the half-ester (IIa) could not be hydrogenated (*vide infra*) to its dihydro derivative, the planned synthesis fell through.



(I)



[IIa : R′=H, R=Et ; IIb : R=R′=H ; IIc : R=R′=Me ; IId : R=H, R′=Me ; IIe : R=Me, R′=H]



(III)

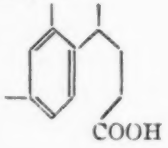
In this connection, a detailed study of some of the reactions of (II) has been made. The Stobbe condensation (Johnson and Daub, "Organic Reactions", John Wiley & Sons Inc., New York, 1951, Vol. 6, p. 2) of diethyl succinate with 2 : 4-dimethylacetophenone gave the half-ester (IIa) ; it was shown that the distilled material was contaminated with the anhydride from the corresponding dicarboxylic acid as well as with the lactone ester (paraconic acid ester). The distilled material was resistant to catalytic reduction with Adams' platinum oxide catalyst either in ethanol or acetic acid at ordinary temperature and pressure.

In view of the above behaviour, it was decided to hydrolyse the half-ester to the pure dicarboxylic acid and to study its reduction. The alkaline saponification always produced a mixture of acids from which one pure isomer could be isolated in 44% yield. In an attempt to establish its structure, its ultraviolet absorption spectrum was investigated, but the compound showed no absorption peak in the 220 mμ to

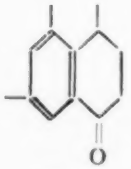
*Part XV, this *Journal*, 1957, **34**, 255.

340 mμ region. Clearly this was a case of steric inhibition of π-π resonance (Brooker *et al.*, *Chem. Rev.*, 1947, **40**, 325 ; Murray and Galloway, *J. Amer. Chem. Soc.*, 1948, **70**, 3867), the expected absorption due to a styrene chromophore (Hirschberg, *ibid.*, 1949, **71**, 3241) or a cinnamic acid system (Romart-Lucas, *Bull. soc. chim.*, 1932, *iv*, **51**, 119 ; 1938, *v*, **5**, 848) being completely suppressed due to twisting of the side chain out of the plane of the benzene nucleus ; this was borne out by a study of the model (Catalin Molecular Models) of the molecule of the dicarboxylic acid (IIb). Furthermore, since the acid was not cleaved by ozonolysis, this method also could not be used for its structural determination. Other methods of structure investigation (Johnson and Daub, *loc. cit.*) were not studied.

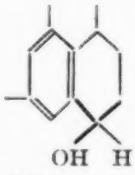
This dicarboxylic acid (IIb) was resistant to catalytic hydrogenation over Adams' catalyst in ethanol or acetic acid at room temperature and pressure. It could not be reduced over Raney nickel (Campbell *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4681) at 50 or 100 atmospheres at 60-70° ; change of the catalyst to Adams' platinum oxide did not induce absorption of hydrogen under these conditions. No hydrogenation was observed over palladium-carbon in ethanol in the presence of perchloric acid (Rosenmund and Karg, *Ber.*, 1942, **75**, 1850). The acid also could not be reduced by chemical methods. Thus sodium amalgam reduction (Klemm and Largman, *J. Amer. Chem. Soc.*, 1954, **76**, 1688) had no effect. Iodine and red phosphorus in acetic acid (Bachmann and Sheehan, *ibid.*, 1940, **62**, 2689 ; cf. Rupe, *Ber.*, 1911, **44**, 585) or Raney-nickel alloy and alkali (Schwenk *et al.*, *J. Org. Chem.*, 1944, **9**, 175) gave a mixture of acids, which on repeated crystallisations gave a product with a constant melting point (184-85°) ; though identical with the melting point of the starting material, it gave a little but definite depression in the melting point on admixture with it. This led us to infer for the time being that the double bond had been reduced ; however, some cyclisation experiments conducted with this material, its anhydride (VIII) or methyl half-ester to obtain (III : R = H or Me) yielded only products typical of the ring-closure of the unsaturated acid (IIb, vide Chart I). Prolonged reduction of the unsaturated acid with phosphorus, iodine and acetic acid for 24 hours furnished γ-(2-*m*-xylyl)-valeric acid (IV), characterised by the preparation of the tetralone (V) and the crystalline tetralol (VI) and their comparison with authentic samples.



(IV)

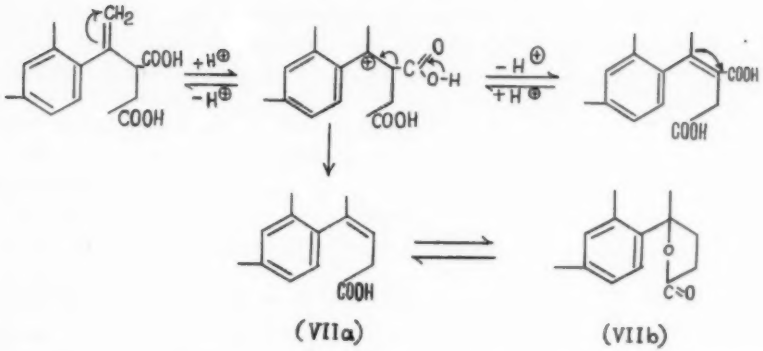


(V)



(VI)

This reaction further demonstrated the hindered nature of the ethylenic linkage in (II) ; decarboxylation took preference over reduction to afford (VIIa) and/or (VIIb) which was readily reducible to γ-(2-*m*-xylyl)-valeric acid (IV). In accordance with the general behaviour of cinnamic acids (Johnson and Heinz, *J. Amer. Chem. Soc.*, 1949, **71**, 2913) and itaconic acids (Johnson *et al.*, *ibid.*, 1947, **69**, 74), this acid-catalysed decarboxylation must have occurred by a S_E^2 mechanism (Brown, *Quart. Rev.*, 1951, **5**, 142).

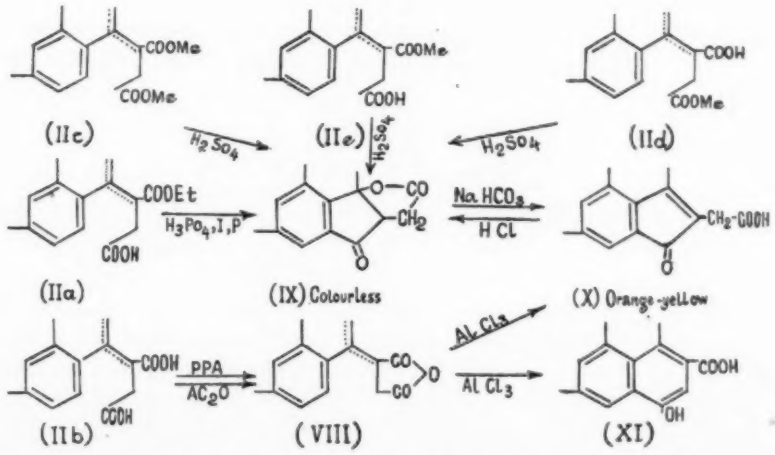


(VIIa) (VIIb)

Attention was next directed to the catalytic hydrogenation of the dimethyl ester (IIc) and the methyl half-esters (IId and IIe) ; however, no success was achieved.

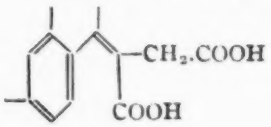
It has been pointed out previously that having been misled by a little depression in the m.p. of the so-called reduced acid on admixture with the starting material (IIb), some ring-closure experiments were carried out. This work, along with the other pertinent reactions are summarised in Chart I. Since the so-called "reduced" acid was shown to be virtually identical with the unsaturated dicarboxylic acid (IIb, m.p. 184-85°), only reactions of the latter acid have been shown (Chart I) and described in the experimental. This depression in the mixed m.p. of (IIb) must be attributed to the formation of some isomeric material under acid-catalysis. It has been shown that the original unsaturated dicarboxylic acid on refluxing with hydrochloric acid in acetic acid gives a material which depresses the melting point; the so-called "reduced" acid is stable to this treatment.

CHART I



The half-ester (IIa) or the unsaturated dicarboxylic acid could not be cyclised with the sodium acetate-acetic anhydride method (Klemm and Largman, *loc. cit.*; Borche,

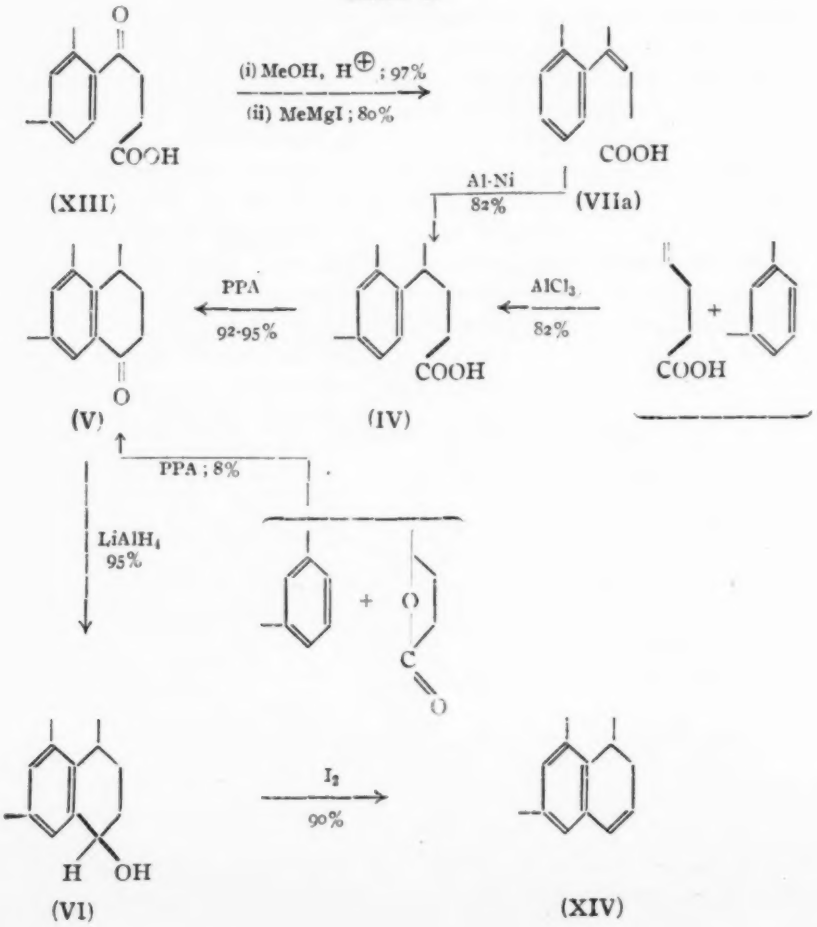
Annalen, 1936, **526**, 1) to the acetate corresponding to (XI). The ready cyclisation of various derivatives (IIc, IIe, IId) of the unsaturated acid to the lactone (IX) indicates that possibly the unsaturated dicarboxylic acid has the structure (XII).



(XII)

4 : 5 : 7-*Trimethyltetralone*-1 (V) *and further Reactions.*—When it had become clear that the Stobbe-condensation route would not work, attention was directed to introduce the *iso*propyl group at C_7 by making use of some suitable reactions of 7 : 8-dihydro-1 : 3 : 8-trimethylnaphthalene (XIV).

CHART II

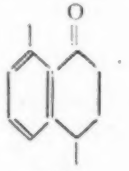


The first step was the preparation of (XIV) (Chart II). This has been recently prepared by Mosby (*J. Amer. Chem. Soc.*, 1952, **74**, 2564). The route to (IV) via γ-(2-*m*-xylyl)-γ-methylvinylacetic acid (VII) was that of Sukh Dev (this *Journal*, 1948, **25**, 79) except that the reduction of (VII) was more conveniently carried out by Raney-nickel alloy and alkali (Schwenk *et al.*, *loc. cit.*). The condensation of allylacetic acid (Eijkmann, *Chem. Weekblad*, 1904, **1**, 421 ; 1905, **2**, 229 ; Mukherji *et al.*, *J. Org. Chem.*, 1953, **18**, 1499 ; cf. Mosby, *loc. cit.*) with *m*-xylene to furnish (IV) in one-step proved simpler. The one-stage preparation of (V), using polyphosphoric acid (PPA) for intermolecular alkylation and acylation (Sukh Dev, *Chem. & Ind.*, 1954, 1071) resulted in a poor yield. The PPA cyclisation of (IV) to give the tetralone (V) in an excellent yield is of interest as this result is in marked contrast with the observation of Mosby (*loc. cit.*). He observed that the acid (IV), prepared by the Friedel-Crafts condensation of γ-valerolactone with *m*-xylene, on cyclisation with PPA, gave 4:6.8-trimethyltetralone-1 (XV) rather than (V), which could be obtained from the same starting material by intramolecular acylation of its acid chloride in the presence of stannic chloride. However, under a variety of conditions studied (Table I) in order to detect this rearrangement with PPA, we have always been able to isolate only (V), the normal cyclisation product*.

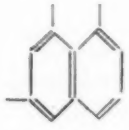
TABLE I

No.	Acid cyclised.	Composition of PPA. H_3PO_4.	P_2O_5.	P_2O_5.	Temp.	Time (mins.).	Yield of (IV).
1.	25.0 g.	131.0 g. (75 c.c.)	125.0 g.	80.4%	100°	60	92-95%
2.	2.5	7.5 g.	12.5	85.5	100°	120	75
3.	0.5	1.75 g.	3.0	85.7	130-35°	15	Identified as 2:4-DNP
4.	1.0	0.64 c.c.	3.0	89.6	135-40°	15	,,

The conditions of the experiment in (4) approximate those of Mosby. This study points to the only possibility that the rearrangement observed by Mosby may be due to some peculiarity of the commercial PPA employed by him.



(XV)



(XVI)

Bromination of 7:8-dihydro-1:3:8-trimethylnaphthalene (XIV) with *N*-bromosuccinimide (Djerassi, *Chem. Rev.*, 1948, **43**, 271) under very mild conditions and the reaction of the crude product with *iso*propylmagnesium bromide gave only 1:3:8-trimethylnaphthalene (XVI).

Mercuric acetate (Treibs and Bast, *Annalen*, 1949, **561**, 165) was found to dehydrogenate (XIV) to (XVI).

* After submission of this paper, Vig and Singh (*Science & Culture*, 1957, **22**, 403) have also failed to observe this rearrangement.

*EXPERIMENTAL

2:4-*Dimethylacetophenone* was prepared according to the method of Claus (*Ber.*, 1886, **19**, 230), but by using 2.2 molecular equivalents of anhydrous aluminium chloride for the condensation. The product had b.p. 118-19°/20 mm, $n_D^{29.5}$ 1.5310, yield 96%.

The *semicarbazone* (sodium acetate method) was obtained as white leaflets from ethanol, m.p. 192-93° (Auwers *et al.*, *Ber.*, 1925, **58**, 48, record m.p. 185-87°).

The 2:4-*dinitrophenylhydrazone* (sulphuric acid method) came out in red needles on crystallisation from benzene-petroleum ether, m.p. 169-70°. (Found: N, 16.93. $C_{16}H_{16}O_4N_4$ requires N, 17.07%).

The Stobbe-condensation: γ-(2-m-*Xylyl*)-β-*carbethoxy*-γ-*methylvinylacetic Acid* (IIa).—To a cooled suspension of potassium butoxide[1] (from butyl[t] alcohol, 350 c.c. and potassium, 23.6 g., 0.605 g. atom), a mixture of acetyl-*m*-xylene (81.4 g., 0.55*M*) and diethyl succinate (143.5 g., 0.825*M*) was added in one lot and refluxed for 2 hours under nitrogen atmosphere and left at room temperature overnight. The reaction mixture, which was light brown in the beginning, became deep brown towards the end. It was worked up by acidifying with HCl (1:1; 110 c.c.) with cooling. The tertiary butanol was distilled off under reduced pressure and to the cooled residue water (400 c.c.) was added. It was made alkaline with sodium bicarbonate (about 70 g.) or 10% ammonium hydroxide and the neutral material was removed by extraction with petroleum ether (25 c.c. × 4). The alkaline extract was treated with decolorising carbon, filtered and the filtrate was cooled and acidified with HCl (1:1), when it gave a thick oily, pale brown liquid which was separated and completely extracted with petroleum ether (30 c.c. × 4) from the aqueous portion and combined with the main lot. The combined extract was washed repeatedly with water (25 c.c. × 4) to remove all traces of mineral acid (the presence of even a trace of mineral acid led to complete polymerisation and loss of material during distillation) and dried (Na_2SO_4). The solvent was removed and the residue (128 g.) fractionated to afford a colorless, viscous liquid, b.p. 170-74°/0.2 mm, 195-98°/1 mm, n_D^{24} 1.5330, yield 83 g. [Found: C, 70.0; H, 7.6. $C_{16}H_{20}O_4$ requires C, 69.6; H, 7.24%].

The distillate (3.3 g.) was taken up in petroleum ether and washed with sodium bicarbonate solution at 0°. Acidification of the cooled bicarbonate extract gave the half-ester (2.5 g.). The neutral petroleum ether solution on evaporation gave a liquid residue, which was digested with water for 1 hour on the steam-bath. After cooling, it was taken up in ether and extracted with aqueous sodium bicarbonate solution, when a solid acid (m.p. 155-60°; 0.3 g., *vide infra*) was isolated on acidification of this extract. Removal of the solvent from the petroleum ether layer gave a trace (about 0.1 g.) of a liquid residue (paraconic acid ester ?).

Saponification of the Half-ester: *Unsaturated Dicarboxylic Acid* (IIb).—The half-ester (15 g.) was refluxed with aqueous NaOH (10 g. in 100 c.c. of water) for 2 hours and diluted with water (300 c.c.), when all the sodium salt went into solution. The clear hot solution was cooled in ice and acidified with cold dilute HCl (1:1).

* All melting and boiling points are uncorrected. Petroleum ether employed was the fraction with the boiling range 40-60°.

The product separated as a thick oil which quickly solidified, m.p. 150-65°, yield 10 8. g. (80%). The product after repeated crystallisations, twice from dilute acetic acid and four times from dilute ethanol, was obtained in colorless microprisms (3.2 g.), m.p. 183.5-84° (with effervescence). It was shown (Sukh Dev, this *Journal*, 1955, **32**, 255) that the gas evolution was due to anhydride formation and not to decarboxylation. [Found: C, 67 44; H, 6.39; N.E., 125. $C_{14}H_{16}O_4$ requires C, 67.74; H, 6.45%; N.E., 124].

The s-*benzylthiuronium salt* was obtained as a white powder, m.p. 148-49°, after two crystallisations from ethanol. [Found: N, 9 66. $C_{30}H_{34}O_4N_4S_2$ requires N, 9.69%).

Dimethyl (IIc) *and Monomethyl* (IId & IIe) *Esters.*—A mixture of the above pure unsaturated acid (m.p. 184°, 2.5 g.), anhydrous methanol (4 c.c.), benzene (5 c.c.) and H_2SO_4 (C P. 0.5 c.c) was refluxed for 10 hours. This was cooled, diluted with water (50 c.c.) and extracted with benzene-ether mixture (1 : 1; 15 c.c. × 3). The combined solvent extract was washed with aqueous sodium carbonate (1%; 10 c.c. × 3) and the alkaline extract reserved for the isolation of the monomethyl ester (*vide infra*). After further washing with brine (10 c.c. × 2) and drying (Na_2SO_4), the solvent was removed and the neutral dimethyl ester (IIc) was purified by distillation as a colorless viscous liquid, b.p. 143-44°/0.8 mm, n_D^{32} 1.5200, yield 1.2 g. (Found: C, 69.2; H, 8.2. $C_{16}H_{22}O_4$ requires C, 69.06; H, 7.92%).

The alkaline washings on acidification gave a solid (m.p. 139-42°; 1 g.) which after three crystallisations furnished white prisms, m.p. 143°, of the monomethyl ester (IId). (Found: C, 68.28; H, 7.6. $C_{15}H_{20}O_4$ requires C, 68.18; H, 7.58%).

When the above esterification was carried out for 3 hours with benzene, the ester (IId m.p. 143°) was obtained exclusively.

For the preparation of the isomeric monom$_e$thyl ester (IIe), the dimethyl ester (5.55 g.) was refluxed with KOH (1.12 g. in water 2 c.c. and methanol 12 c.c.) for 3 hours. The reaction mixture was diluted with water (150 c.c.) and extracted with ether (15 c.c. × 4). Acidification of the aqueous layer produced a thick oil which was extracted with benzene (20 c.c. × 2). The combined benzene extract was washed with water. On removal of the solvent, a viscous residue (4.2 g.), which failed to solidify, was left. This was used as such for the cyclisation experiments.

The dicarboxylic acid (m.p. 184-85°), obtained from the "reduction" experiments (*ii*) and (*iii*) (*vide infra*) gave results exactly identical with those described above.

Reductive Decarboxylation to γ-(2-m-Xylyl)-valeric Acid (IV).—The dicarboxylic acid (10 g.) was refluxed for 26 hours with a mixture of red phosphorus (10 g.) and iodine (10 g.) in glacial acetic acid (100 c.c.) containing water (10 c.c.). The cooled reaction mixture was filtered and from the filtrate the solvent was removed under reduced pressure from a steam-bath. The residue was poured into water (150 c.c.) containing sodium bisulphite (10 g.). A liquid separated out which was taken up in ether (20 c.c. × 4). The combined ether extract was washed with water (10 c.c. × 2), followed by aqueous sodium bicarbonate (5%; 20 c.c. × 3). The alkaline extracts were washed with ether and then acidified. The product was taken up in

benzene (20 c.c. × 3) and washed with water. The solvent was flashed off and the residue fractionated to afford a colorless viscous liquid, b.p. 143-48/0.5 mm, $n_D^{32.6}$ 1.5185, yield 7.0 g. (90%). The physical properties are almost identical with those of an authentic sample (*vide infra*).

The PPA (from P_2O_5 3 g. and H_3PO_4 2 c.c.) cyclisation of the above acid (1 g.) at 100° for 2 hours furnished 4 : 5 : 7-*trimethyltetralone*-1 (V), b.p. 139-40°/4 mm, n_D^{25} 1.5580, yield 0.75 g. (82%), identified as its 2 : 4-*dinitrophenylhydrazone*, fine red needles, m.p. 232-33° ; mixed m.p. with an authentic sample (*vide infra*) was not depressed. The ketone was further identified by its $LiAlH_4$ reduction to the crystalline *tetralol* (VI) (*vide infra*) ; m.p. and mixed m p. with an authentic sample, 109-110°.

Reduction Experiments.—A few typical attempts at reducing (IIb) or its derived esters are described below :

(*i*). A freshly distilled sample of the half-ester (IIa, 10 g.) in ethanol (30 c.c.) or acetic acid (100 c.c.) was shaken with pre-reduced Adams' platinum oxide catalyst (250 mg.) in an atmosphere of hydrogen ; no absorption of hydrogen was observed during several hours. The unsaturated dicarboxylic acid (IIb) behaved in the same manner.

The dicarboxylic acid (IIb, 5 g.) in ethanol (20 c.c.) was stirred in a stainless steel autoclave with Raney-nickel (1 g.) or PtO_2 catalyst (80 mg.) at 50 or 100 atmospheres at 60-70° for 6 hours. No reduction took place and the starting material was recovered. The esters (IIc, IId and IIe) behaved similarly.

(*ii*). The half-ester (IIa, 4.5 g.) was refluxed with iodine (4.5 g.), red phosphorus (4.5 g.) and acetic acid (glacial acetic acid 90 c.c. and water 9 c.c.) for 2 hours and worked up in the usual way. Four recrystallisations of the crude material (3.5 g., m.p. 170-75°) from dilute ethanol (1 : 1) gave white microprisms (1.2 g.), m.p 184-85° with effervescence ; the m.p. could not be raised on further recrystallisation ; mixed m.p. with the unsaturated dicarboxylic acid (IIb) of m.p. 183.5-84° was 175-80°. [Found : C 67.29 ; H, 7.21 ; equiv., 124.4 (titration method), 124.1 (Ag salt method). $C_{14}H_{16}O_4$ requires C, 67.74 ; H, 6.45% ; equiv., 124].

The *s-benzylthiuronium salt* separated from ethanol as a white powder, m.p. 154° ; mixed m.p. with the *s*-benzylthiuronium salt (m.p. 148-49°), prepared from the unsaturated dicarboxylic acid (IIb), was 145-53°. [Found : N, 10.2. $C_{30}H_{36}O_4N_4S_2$ requires N, 9.69%].

The unsaturated acid (IIb) behaved similarly.

(*iii*). The half-ester (5.5 g.) in NaOH (10 g.) in water (150 c.c.) was treated with Raney-nickel alloy (3 g.) and worked up as described for the preparation of the acid (IV). The crude product (4.0 g.) had m.p. 150-65°, which after three crystallisations from ethanol gave white microprisms, m.p. 184-85° (efferv.) ; mixed m.p. with a sample from experiment (*ii*) was undepressed, while with the unsatured dicarboxylic acid, it was 175-80°. No material with a constant m.p. could be isolated from the mother-liquors.

The unsaturated dicarboxylic acid (IIb) on similar treatment with Raney-nickel alloy gave the same results.

Ozonolysis of the unsaturated dicarboxylic acid (IIb) (0.8 g.), when carried out according to a known procedure (Sukh Dev, *loc. cit.*), gave back the starting material unchanged.

Cyclisations to (IX) *and* (X)

(*i*). *Sulphuric Acid Cyclisation of* (IIc, IId & IIe).—Each of the three methyl esters (0.5 g.) was treated separately in the cold with H_2SO_4 (conc., 0.5 c.c.). The mixture was left overnight (15 hours) at room temperature (25°) and was diluted with cold water (10 c.c.). The solution was extracted with ether (10 c.c. × 3) and the neutral ether extracts obtained after washing with aqueous sodium bicarbonate and water gave a white solid on removal of the solvent. On two crystallisations from methanol, the *γ-lactone of 3:4:6-trimethyl-*$\Delta^{2:3}$*-inden-1-one-2-acetic acid* (IX) was obtained as beautiful, colorless, flat needles, m.p. 148-49°, yield 0.15-0.17 g. [Found: C, 72.58; H, 6.47. $C_{14}H_{14}O_3$ requires C, 73.04; H, 6.09%].

The *2:4-dinitrophenylhydrazone* was crystallised from ethyl acetate in orange-red leaflets, m.p. 265-66° (decomp.). [Found: N, 13.48. $C_{20}H_{17}O_6N_4$ requires N, 13.66%].

When the above lactone (IX, 0.15 g.) was heated with an aqueous solution of sodium bicarbonate (5%, 10 c.c.) on a boiling water-bath for 1 hour, a clear deep orange solution was obtained. Acidification with cooling afforded an orange-yellow solid. Two crystallisations from dilute methanol yielded the beautiful yellow needles of *3:4:6 trimethyl-*$\Delta^{2:3}$*-inden-1-one-2-acetic acid* (X), m.p. 175-76°, yield 0.1 g. [Found: C, 72.68; H, 6.07. $C_{14}H_{14}O_3$ requires C, 73.04; H, 6.09%].

Lactonisation of the indenone-acetic acid (X, 0.15 g.) was effected by refluxing it with a mixture of acetic acid (2 c.c.) and HCl (2 c.c.) for 5 hours. On dilution with water (25 c.c.), a white crystalline solid was obtained. This was suspended in ice-cold aqueous sodium bicarbonate solution (2%) for a few minutes, filtered, washed with water and crystallised from ethanol to furnish colorless flat needles (0.1 g.), m.p. 148°, undepressed by (IX).

(*ii*). *Action of Iodine and Red Phosphorus on the Half-ester* (IIa) *in Syrupy Phosphoric Acid.*—In an experiment designed to reduce and cyclise the half-ester (IIa, 5.2 g.), in one step (Sukh Dev, this *Journal*, 1948, **25**, 323), a neutral crystalline solid was obtained. This on three crystallisations from ethanol gave pure (IX), m.p. 148°, yield 1 g. From the acidic part an acid was isolated as its calcium salt (0.6 g.), which on decarboxylation and dehydrogenation with sulphur yielded a product (30 mg.), which failed to form a trinitrobenzene complex.

(*iii*). *Action of Aluminium Chloride on the Unsaturated Dicarboxylic Acid Anhydride* (VIII).—The anhydride was prepared by heating the dicarboxylic acid (IIb, 1 g.) with acetic anhydride (1 c.c.) at 130-35° for 1 hour. The excess acetic anhydride and acetic acid were removed under suction from a steam-bath and the residue fractionated to provide the *anhydride* as a viscous, pale yellow liquid, b.p. 168-70°/1 mm. n_D^{25} 1.5640, yield 0.84 g. (90%). This was directly used in the next step.

The anhydride (1.8 g.) in thiophene-free benzene (10 c.c.) was treated with anhydrous aluminium chloride (2.2 g.) at 0° for 15 hours and then allowed to attain room temperature during 2 hours. The reaction mixture was poured on ice (100 g.) and HCl (10 c.c.), when an orange-yellow solid separated. This was taken up in ether (25 c.c. × 3) and extracted with aqueous sodium carbonate (10%, 15 c.c. × 3). On acidification, an orange-coloured heavy oil separated, which slowly solidified, m.p. 155-65°, yield 1.8 g. This was refluxed with benzene (150 c.c.) and the insoluble material (0.25 g., m.p. 210-20°) was collected and crystallised four times from dilute alcohol to yield colorless prisms (0.1 g.), m.p. 223.5-24°. This gave a reddish brown colour with aqueous ferric chloride in ethanol. It analysed for 4 : 5 : 7 *trimethyl-3-carboxy-α-naphthol* (XI). [Found: C, 72.93; H, 5.98. $C_{14}H_{14}O_3$ requires C, 73 04; H, 6.09%].

The benzene-soluble portion gave a solid (0.7 g., m.p. 168 72°) on concentration. Two crystallisations from ethanol furnished the pure compound (X) as yellow needles (0.4 g.), m.p. 175°.

When the real nature of the dicarboxylic acid (m.p. 184-85°) produced in the reduction experiments (*ii* and *iii*) had not been established, its cyclisation (Horning and Walker, *J. Amer. Chem. Soc.*, 1952, **74**, 5147; cf. Urban and Beavers, *ibid.*, 1954, **76**, 3042) with PPA was investigated. The acid (2.5 g.) on treatment with PPA (from P_2O_5 7 g. and H_3PO_4 4 c.c.) at 100° for 1 hour gave a very dark product, which did not furnish any pure material on working up. However, when the heating was carried out for just 8 minutes and then worked up into acidic and neutral parts, only a neutral product was obtained as a thick colorless residue. This did not react with 2 : 4-dinitrophenylhydrazine reagent, but went into solution on warming with aqueous sodium carbonate; acidification yielded the starting material (2 g.), m.p. and mixed m.p., 184-85°. This indicated clearly that the PPA had just converted the acid into its anhydride (VIII).

β-(2-m-Xyloyl)-propionic acid (XIII) was prepared as described by Sukh Dev (this *Journal*, 1948, **25**, 69).

The *semicarbazone* (sodium acetate method) was crystallised from ethanol in white shining plates, m.p. 177-78°. [Found: N, 15.54. $C_{13}H_{17}O_3N_3$ requires N, 15.97%].

The *s-benzylthiuronium salt* was obtained as a white powder from ethanol, m.p. 138.5°. [Found: N, 7.71. $C_{20}H_{24}O_3N_2S$ requires N, 7.53%].

Methyl β-(2-m-Xyloyl)-propionate.—A mixture of the above acid (62 g., 0.3*M*), methanol (93 c.c.), benzene (120 c.c.) and H_2SO_4 (C.P. 14 c.c.) was refluxed for 12 hours and worked up in the usual way to afford the ester as a liquid, b.p. 168-69°/6 mm, n_D^{27} 1.5215, yield 97% (Sukh Dev, *loc. cit.*, record b.p. 151-52° at 2.5 mm, yield 87.5%).

The *semicarbazone* was crystallised from ethanol twice to furnish thick white prisms, m.p. 146-47°. [Found: N, 15.01. $C_{14}H_{19}O_3N_3$ requires N, 15.16%].

γ-(2-m-Xylyl)-valeric Acid (IV)

(*i*). *From γ-(2-m-Xylyl)-γ methylvinylacetic Acid* (VII).—To a warm solution of NaOH (20 g. in 150 c.c. water), taken in a 1-litre 3-necked flask fitted with a stirrer,

the crude unsaturated acid (VII, 20.4 g., 0.1*M*) (Sukh Dev, *loc. cit.*) was added. This was reduced with aluminium nickel alloy (10 g.) by following a procedure described elsewhere (Sukh Dev, *ibid.*, 1955, **32**, 518). The acid (IV) was obtained as a colorless viscous liquid, b.p. 150-52°/1 mm, n_D^{25} 1.5200, yield 16.68 g. (82%) (Sukh Dev, *loc. cit.*, records b.p. 170-73°/3 mm).

The s-*benzylthiuronium salt* was crystallised from dilute ethanol as a white microcrystalline powder, m.p. 125-26°. [Found: N, 7.46. $C_{21}H_{28}O_2N_2S$ requires N, 7.53%].

(*ii*). *By the Condensation of Allylacetic Acid with* m-*Xylene*.—Allyl chloride was condensed with diethyl malonate according to the procedure of Linstead and Rydon (*J. Chem. Soc.*, 1933, 580) to afford the diethyl allylmalonate (b.p. 102-103°/10 mm, n_D^{27} 1.4285, yield 60%). This was hydrolysed by alkali (Linstead and Rydon, *loc. cit.*) to the malonic acid which decarboxylated at 180-220° under slight suction to give the allyacetic acid (b.p. 182-84°, yield 65-75%). Its s-*benzylthiuronium salt* was crystallised from water in white lustrous leaflets, m.p. 153-54°. [Found: N, 10.52. $C_{13}H_{18}O_2N_2S$ requires N, 10.60%].

To a mixture of allylacetic acid (5 g., 0.05*M*) and *m*-xylene (10.6 g., 0.1*M*), taken in a 3-necked flask fitted with a condenser, stirrer and guard tube connected with a gas trap, powdered anhydrous aluminium chloride (7.4 g., 0.055*M*) was added during 30 minutes with stirring. The temperature slowly rose. At the end of the addition, the reaction mixture was heated so that the *m*-xylene refluxed gently for 5 to 10 minutes. The reaction mixture was cooled and poured on crushed ice (100 g.) and HCl (20 c.c.). The product was taken up in benzene (25 c.c. × 3), washed with brine (20 c.c × 2) and dried (Na_2SO_4). The solvent was removed and the residue fractionated to give (IV) as a thick colorless oil b.p. 159-164°/2 mm, n_D^{30} 1.5125, yield 75%.

The s-*benzylthiuronium salt* (m.p. 125-26°), prepared from this sample, did not depress the m.p. of the product from experiment (*i*).

4:5:7-*Trimethyltetralone*-1 (V)

(*i*). *By the Cyclisation of* γ-(2-m-*Xylyl*)-*valeric Acid* (IV).—A mixture of P_2O_5 (125 g.) and syrupy H_3PO_4 (85%, *d* 1.75, 75 c.c.) was heated with stirring on a boiling water-bath for 2 hours. The above γ-(2-*m*-xylyl)-valeric acid (25 g.) was added all in one lot to the PPA obtained, made homogeneous by stirring for 5-10 minutes and maintained at 100° for 1 hour. The reaction mixture was cooled and poured on crushed ice (250 g.) containing some ether (50 c.c.) and extracted with benzene (25 c.c. × 4). The combined benzene extract was washed with brine (20 c.c.), followed by aqueous sodium bicarbonate (10%, 20 c.c × 2) and finally with brine (15 c.c. × 2). The solvent was removed and the residue fractionated, b.p. 125-30°/2 mm, $n_D^{24\cdot5}$ 1.5585, yield 92-95%.

The 2:4-*dinitrophenylhydrazone* after two crystallisations from benzene was obtained in deep red needles, m.p. 232°. Mixed m.p. with the sample obtained by the Friedel-Crafts intramolecular acylation of the acid chloride (Sukh Dev, *loc. cit.*) was not depressed.

(ii). By the Simultaneous Condensation and Cyclisation by PPA between γ-Valerolactone and m-Xylene.—A mixture of *m*-xylene (2.12 g., 0.02*M*) and γ-valerolactone (2 g., 0.02*M*) was stirred with polyphosphoric acid (P_2O_5 13 g., H_3PO_4 7.8 c.c.) at 100° for one hour. It was worked up as described already and the crude tetralone was obtained in 8% yield. It was characterised as 4 : 5 : 7-trimethyltetralone-1 by the preparation of the 2 : 4-dinitrophenylhydrazone, m.p. 232°. Mixed m.p. with an authentic sample was not depressed.

4 : 5 : 7-*Trimethyltetralol*-1 (VI) was prepared essentially according to the method of Mosby (*loc. cit.*) as white glistening leaflets (benzene-petroleum ether), m.p. 108-109°, yield 95% (Mosby records, m.p. 108-109°, yield 84%).

4 : 5 : 7-*Trimethyl*-3 : 4-*dihydronaphthalene* (XIV).—The above tetralol (4 g.) was dehydrated with iodine (20 mg.) as described by Mosby (*loc. cit.*) and purified by passage through a column of activated alumina (20 g.), b.p. 90-92°/2 mm, n_D^{28} 1.5590, d_{16}^{28} 0.9648, M_D 57.72 (calc. 55.98 ; $E\,\Sigma_D$ 1.01), yield 3.21 g. (90%). (Mosby records b.p 64-66°/0.15 mm, n_D^{24} 1.5616).

Action of Mercuric Acetate on (XIV) : *Dehydrogenation to* 1 : 3 : 8-*Trimethylnaphthalene.*—A mixture of the hydrocarbon (2.6 g., 0.015*M*) and mercuric acetate (4.8 g., 0.015*M*) was heated for 5 hours at 150° and the reaction mixture worked up in the usual way (Treibs and Bast, *loc. cit.*). The product (0.9 g.) had b.p. 96-99°/1.5 mm, n_D^{24} 1.5665 and it was characterised as 1 : 3 : 8-*trimethylnaphthalene* by the preparation of (*i*) its orange-red *picrate*, m.p. 125° (Mosby, *loc. cit.*, records m.p. 125-125.5°), the *trinitrofluorenone complex*, orange-red microneedles (acetic acid), m.p. 144-45° (Mosby, *loc. cit.*, records m.p. 142.5-143°) [Found : N, 8.85. $C_{26}H_{19}O_7N_3$ requires N, 8.66%] and (*iii*) the *trinitrobenzene complex*, yellow needles (80% acetic acid), m.p. 145° [Found : N, 10.82. $C_{19}H_{17}O_6N_3$ requires N, 10.97%].

Bromination of (XIV) *and Attempted Condensation with* iso*Propylmagnesium Bromide.*—Treatment in ethereal (15 c.c.) solution of the crude material, obtained by bromination of (XIV, 1.9 g.) with *N*-bromosuccinimide (2.4 g.) in dry CCl_4 (10 c.c.) in presence of benzoyl peroxide (0.5 g.) at laboratory temperature, with *iso*propylmagnesium bromide (from Mg 0.64 g., *iso*propyl bromide 3 c.c. and ether 30 c.c.) at room temperature under nitrogen atmosphere and working up in the usual way yielded mainly the 1 : 3 : 8-*trimethylnaphthalene*, m.p. 48°, obtained in fine white needle-shaped crystals from ethanol (Mosby, *loc. cit.*, records a m.p. of 47.6-48.2°). It was further characterised by the preparation of its TNB complex, m.p. 145° ; mixed m.p. was undepressed with the sample obtained above.

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RELATIONSHIP BETWEEN BASICITY OF ACIDS AND CONDUCTANCE IN AQUEOUS SOLUTIONS

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From Onsager's conductance equation, simplified relations for unsymmetrical electrolytes have been obtained, connecting conductance of the salts with the basicity of acids, from which the former are derived. These relations permit of drawing conclusions regarding basicity and change in conductance, similar to Ostwald's empirical rule. It is also possible to lay down an acidity rule for the acidities of simple alkalies from a consideration of these relations.

The equivalent conductance data of sodium and potassium salts of different acids and the basicities of the latter were correlated by Ostwald (*Z. physikal. Chem.*, 1887, **1**, 105) in the form of an empirical relation, viz.,

$$\lambda_{1024} - \lambda_{32} = 10.8\, b \qquad \ldots \qquad \ldots \quad (1)$$

where 'b' is the basicity of the acid and λ terms represent equivalent conductances of the sodium or potassium salts at 1024 and 32 litres dilutions. The failure of the relation in many cases is associated with the selection of the two arbitrary dilution limits—a range over which the conductance of sodium salts of any two monobasic or polybasic acids may not exhibit identical nature of decline.

The quantitative description of the change in electrical conductance of electrolyte solutions with concentration has been given in the form of empirical relations by Kohlrausch ("Leitvermogen der Elektrolyte"), Walden (*Z. physikal. Chem.*, 1924, **108**, 341), Jones and Dole (*J. Amer. Chem. Soc.*, 1930, **52**, 2245), and Lorenz (*Z. anorg. Chem.*, 1919, **108**, 191 ; 1920, **114**, 209). None of these equations proved successful over wide concentration limits.

Onsager's theoretical extension (*Physikal. Z.*, 1927, **28**, 277) of the Debye-Hückel conductance equation is

$$\lambda = \lambda_0 - \left[\frac{29.15}{(DT)^{1/2}\eta}(Z_+ + Z_-) + \frac{9.90 \times 10^5}{(DT)^{3/2}}\omega\lambda_0\right]\sqrt{C(Z_+ + Z_-)} \qquad \ldots \quad (2)$$

where, $\omega = 2qZ_+Z_-/(1+\sqrt{q})$; $q = Z_+Z_-(\lambda_+ + \lambda_-)/(Z_+ + Z_-)(\lambda_+Z_- + \lambda_-Z_+)$.

Z and λ terms denote valency and equivalent conductance with subscripts + and − characterising the nature of the ions. D, T and η represent dielectric constant, temperature and viscosity coefficient of the solution respectively. For a uniunivalent electrolyte (type NaCl) equation (2) yields

$$\lambda = \lambda_0 - \left[\frac{29.15}{(DT)^{1/2}\eta} \times 2 + \frac{9.90 \times 10^5}{(DT)^{3/2}}\lambda_0(2-\sqrt{2})\right]\sqrt{C \times 2} \qquad \ldots \quad (3)$$

or $$\lambda = \lambda_0 - [A + B\lambda_0]\sqrt{C \times 1} \qquad \ldots \quad \ldots \quad \ldots \quad 4(a)$$

where $A = \frac{29.15}{(DT)^{1/2}\eta} \times 2\sqrt{2}$ and $B = \frac{9.90 \times 10^5}{(DT)^{3/2}}(2-\sqrt{2})\sqrt{2}$.

For a ternary electrolyte (Na_2SO_4), Onsager's equation takes the form :

$$\lambda = \lambda_0 - [0.915A + 1\,03B\omega\lambda_0]\sqrt{C} \times 2 \quad \ldots \quad \ldots \quad 4(b)$$

Similarly, for a quaternary electrolyte (type Na_3PO_4) and for a still one unit higher unsymmetrical electrolyte (type $Na_4P_2O_7$), equation (2) yields respectively :

$$\lambda = \lambda_0 - [0.94A + 0.8B\omega\lambda_0]\sqrt{C} \times 3 \quad \ldots \quad \ldots \quad 4(c)$$

and

$$\lambda = \lambda_0 - [0.99A + 0.67B\omega\lambda_0]\sqrt{C} \times 4 \quad \ldots \quad \ldots \quad 4(d)$$

The presence of $\lambda_+Z_- + \lambda_-Z_+$ term in ω of equation (2) prevents from utilising equation (4) unless λ_+ and λ_- of ions in finite concentration be known. We therefore have attempted to find out simplified forms of equations 4 (b, c, d) after some sacrifice of strict rigour.

With $(\lambda_+Z_- + \lambda_-Z_+) = \frac{1}{2}\{(Z_+ + Z_-)(\lambda_+ + \lambda_-) + (Z_- - Z_+)(\lambda_+ - \lambda_-)\}$, the form of q (involved in ω of equation 2), becomes

$$q = \frac{Z_+Z_-}{(Z_+ + Z_-)\left\{\frac{1}{2}(Z_+ + Z_-) + \frac{1}{2}(Z_- - Z_+)\frac{\lambda_+ - \lambda_-}{\lambda_+ + \lambda_-}\right\}} \quad \ldots \quad 5(a)$$

For a unibivalent electrolyte (Na_2SO_4)

$$q = \frac{4}{9}\left[1 + \frac{1}{3} \cdot \frac{\Delta\lambda_0 - \Delta x}{\lambda_0 - (x_+ + x_-)}\right]^{-1}$$

where x terms with their subscripts denote the amount of suppressed conductance of the respective ions due to interionic effects in solutions of finite concentration.

Neglecting higher power terms and remembering $\Delta x \ll [\lambda_0 - (x_+ + x_-)]$

$$q \approx \frac{4}{9}\left[1 - \frac{1}{3} \cdot \frac{\Delta\lambda_0}{\lambda_0 - (x_+ + x_-)}\right]$$

Since x terms are small compared to λ_0 in dilute solutions, we neglect $(x_+ + x_-)$ terms in comparison with λ_0 and restrict ourselves to dilute solutions of electrolytes. (The validity of the assumption suffers more and more with increasing concentration and increasing valency of the anion in the unsymmetrical electrolyte). Hence,

$$q \approx \frac{4}{9}\left(1 - \frac{1}{3}\frac{\Delta\lambda_0}{\lambda_0}\right) \quad \ldots \quad \ldots \quad 5(b)$$

Similarly, for a quaternary electrolyte of the type Na_3PO_4 and for a still higher magnitude unsymmetrical electrolyte (type $Na_4P_2O_7$), relation 5 (a) yields respectively :

$$q \approx \frac{3}{8}\left(1 - \frac{1}{2}\cdot\frac{\Delta\lambda_0}{\lambda_0}\right) \quad \ldots \quad \ldots \quad 5(c)$$

and

$$q \approx \frac{8}{25}\left(1 - \frac{3}{5}\cdot\frac{\Delta\lambda_0}{\lambda_0}\right) \quad \ldots \quad \ldots \quad 5(d)$$

The ω terms in relations 4 (b, c, d) involve q, defined by relations 5 (b, c, d), which are constant for any electrolyte. Hence, 4 (a, b, c, d) predict linear variation of equivalent conductances with square root of concentrations. Experimental data, selected at random (Conway, "Electrochemical Data", Elsevier Publishing Company) for different salts of organic and inorganic acids of different basicities bear this out in lower ranges of concentration. While the extent of agreement is more for salts of low valent anions, a value of $\sqrt{C} = 0.1$ may be set as a rough maximum limit at which all electrolytes with univalent cations practically obey the linearity demanded by the relations. [Deviations are observed with some electrolytes, e.g., $K_4Fe(CN)_6$]. The equations 4 (a, b, c, d) can be used for any salt for the determination of the basicity of the acids from which the former are derived. The numerical figures outside parenetheses in these relations represent the corresponding basicities. A guiding approximate rule relating change in λ with b, can, however, be obtained from these, if we insert in the latter an average value of λ_0 and $\Delta\lambda_0/\lambda_0$ for all types of sodium salts of acids. The latter consist, on the one hand, of organic anions with minimum average conductance of 30 mhos cm^2 at 25° and on the other, of inorganic anions with limiting conductance of 80 mhos cm^2 at 25°. (Anions with λ_0 values lying on either side of these limits are also met with, but their numbers are comparatively few). Thus average λ_0 value of sodium salt is equal to 105 mhos cm^2 at 25° and $\Delta\lambda_0/\lambda_0$, while varying from $+1/4$ to $-3/13$. yields an average of nearly 0.01. When this value is considered in conjunction with relations 5 (b, c, d), the ω terms in equations 4 (b, c, d) are evaluated as 1.06, 1.38 and 1.62 respectively. Hence at 25°, with $\eta = 0.895$ centipoise and $D = 78.5$, we have from 4 (a, b, c, d):

For univalent sodium salt		$\lambda_0 - \lambda = (60 + 0.23\,\lambda_0)\sqrt{C}\,b_1$	... (6)
unibivalent	...	$\lambda_0 - \lambda = (54.9 + 0.25\lambda_0)\sqrt{C}\,b_2$	
unitervalent	...	$\lambda_0 - \lambda = (56.4 + 0.25\lambda_0)\sqrt{C}\,b_3$	
unitetravalent	...	$\lambda_0 - \lambda = (59.4 + 0.25\lambda_0)\sqrt{C}\,b_4$	

where b terms denote basicities.

Therefore, instead of choosing two arbitrary dilution limits of 1024 and 32 litres, it is preferable to select the more fundamental limits of infinite and 100 litres ($C = 0.01\,N$) —a range over which relations (6) quantitatively describe the variation of λ with $\sqrt{C}$ in formulating a general basicity rule. As already stated, with $\lambda_0 = 105$ mhos cm^2 and $C = 0.01N$, relations (6) give at 25°, for

(*i*)	uniunivalent sodium salt	$\lambda_0 - \lambda = 8.41\ b_1$	
(*ii*)	unibivalent ...	$\lambda_0 - \lambda = 8.12\ b_2$	... ... (7)
(*iii*)	unitervalent ...	$\lambda_0 - \lambda = 8.27\ b_3$	
(*iv*)	unitetravalent ...	$\lambda_0 - \lambda = 8.56\ b_4$	

From equations (7) follows the basicity rule, viz., "The difference in equivalent conductances of sodium salts of any acid at infinite and 100 litres dilutions is nearly 8.3 times the basicity of the acid." Table I shows the agreement for a number of acids at 25°.

TABLE I

Na salt of.	$\lambda_2 - \lambda_{100}$ (in mhos cm²).	Basicity of acid Calculated from Eq. (4).	Approximate rule.	Actual.
HCl	7.94	0.87	0.95	1
HI	7.70	0.86	0.93	1
Acetic	7.24	0.89	0 87	1
Butyric	6.94	0.88	0.83	1
$HMnO_4$	7.80	0.91	0.94	1
H_2SO_4	17.46	1.95	2.10	2
Oxalic	15.60	1.78	1.88	2

N. B. The different ionic conductances or λ values, needed in compiling the above table, have been obtained from (*i*) International Critical Tables, McGraw and Hill Book Company, (*ii*) Conway, *loc. cit.*, (*iii*) R. Gurney, "Ionic Processes in Solution," International Chemical Series and (*iv*) Harned, "Physical Chemistry of Electrolytic Solutions".

Relations 4 (a, b, c, d), obtainable from Onsager's equation, can also be utilised for the determination of acidities of simple bases. These equations will hold good for chlorides of different alkalies representing uni-uni, bi-uni, tri-uni and tetra-univalent electrolytes. The cations of such bases have λ_0 values lying mostly between 30 and 75 mhos cm². ($\lambda^0_{K^+} = 74$ mhos cm² and $\lambda^0_{Et_4N^+} = 32$ mhos cm²). Hence, average λ_0 and $\Delta\lambda_0/\lambda_0$ values of the chlorides of simple alkalies are 128 mhos cm² and −0.217 respectively at 25°. Using these values and following the procedure adopted in arriving at equations (7), we have at 25° the following relations for

(*i*)	uni-univalent chloride	$\lambda_0 - \lambda = 8.94\ a_1$	
(*ii*)	bi-univalent ...	$\lambda_0 - \lambda = 8.52\ a_2$	... ... (8)
(*iii*)	tri-univalent ...	$\lambda_0 - \lambda = 8\ 63\ a_3$	

where "*a*" terms represent acidities of the bases from which the chlorides are derived. A generalisation, like the basicity of acids, can also be made for the acidities of alkalies as follows:

"The difference in equivalent conductances of chloride of an alkali at infinite and 100 litres dilutions is nearly 8.7 times the acidity of the alkali." Experimental data, recorded in Table II, corroborate it fairly well.

TABLE II

Chloride derived from.	$\lambda_0 - \lambda_{100}$ (in mhos cm^2).	Acidity of the base from Approximate rule.	Actual.
LiOH	7.71	0 88	1
NaOH	7.94	0.91	1
KOH	8 59	0.98	1
NH_4OH	8.43	0.97	1
$Ca(OH)_2$	15.48	1.78	2
$Sr(OH)_2$	15.51	1.78	2
$Ba(OH)_2$	15.04	1.84	2
$Mg(OH)_2$	14.85	1.70	2

Although more stress is laid on the above two approximate rules, it is nevertheless possible to deduce Ostwald's empirical relation from equations (6). At 32 litres and 1024 litres dilutions, the values of $\sqrt{C}$ are 0.17 and 0.031 respectively. With $\lambda_0 = 105$ mhos cm^2, as already stated, and these two values of C, the following relations will hold good for any uniunivalent sodium salt:

$$\lambda_0 - \lambda_{32} = 84.1 \times 0.17\, b_1$$

$$\lambda_0 - \lambda_{1024} = 84.1 \times 0.031\, b_1$$

whence, $$\lambda_{1024} - \lambda_{32} = 11.68\, b_1 \quad \ldots \quad \ldots \quad \ldots \quad 9(a)$$

Similarly, for uni-bi-, uni-tri- and unitetravalent sodium salts, the following can be obtained:

$$\lambda_{1024} - \lambda_{32} = 11.28\, b_2 \quad \ldots \quad \ldots \quad \ldots \quad 9(b)$$

$$\lambda_{1024} - \lambda_{32} = 11.49\, b_3 \quad \ldots \quad \ldots \quad \ldots \quad 9(c)$$

$$\lambda_{1024} - \lambda_{32} = 11.89\, b_4 \quad \ldots \quad \ldots \quad \ldots \quad 9(d)$$

Hence, on the average, we have

$$\lambda_{1024} - \lambda_{32} = 11.58\, b \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

which, in essence, represents the Ostwald basicity rule. Many of the sodium salts, especially those of the higher valent type, do not obey the nature of decline in λ up to 32 litres dilution limit, as is expected from equations (4). This tends to make equation (10), derivable fundamentally from Onsager's equation, inapplicable to such sodium salts.

It may be noted that relations (7) and (8) and the generalisations based on them have been derived for systems at 25°. For work at other temperatures, the corresponding values of A, B, ω and λ_0 have to be inserted in equations 4 (a, b c, d) in deducing the relations similar to (7) or (8) and phrasing the corresponding approximate rules.

The use of Onsager's equation for the determination of λ_0 of electrolytes has long been known. The relations (7) and (8), which stem from the former, can likewise be used for the approximate evaluation of λ_{0-} and λ_{0+} respectively of ions, which are otherwise difficult to measure because of the accompanying effect of hydrolysis with increasing dilution of the corresponding sodium or the chloride compound, e.g., Na_3PO_4 or $AlCl_3$. A table is given here in which the tentative values of several ion conductances, calculated from relations (7) or (8), are shown.

TABLE III

$\lambda^0_{Na^+} = 50.1$ mhos cm^2. $\lambda^0_{Cl^-} = 76.0$ mhos cm^2. $T = 25^\circ$

Ion	Compound considered.	λ_{100} (in mhos cm^2).	λ_c (mhos cm^2)	(Eqns).	$\lambda^0_- = \lambda_0 - \lambda_0 Na^+$ mhos cm^2.	$\lambda^0_+ = \lambda_0 - \lambda_0 Cl^-$ mhos cm^2.	Lit. data available.
PO_4^{3-}	Na_3PO_4	118.6	143.40	(7iii)	93.3	...	...
SeO_4^{2-}	Na_2SeO_4	109.4	125.60	(7ii)	75 5	...	...
$Cr_2O_7^{2-}$	$Na_2Cr_2O_7$	102.5	118.74	(7ii)	68.6	...	...
HCO_3^-	$NaHCO_3$	88.1	96.51	(7i)	46.4	...	44.5 *
Succinate	Na_2 succinate	94.3	110.50	(7ii)	60.4	...	...
La^{3+}	$LaCl_3$	115.9	141.70	(8iii)	...	65.7	69.5† (72.0)‡
Al^{3+}	$AlCl_3$	117.0	142.80	(8iii)	...	66.8	...
Cu^{2+}	$CuCl_2$	114.9	131.90	(8ii)	...	55 9	54.0*

* Conway, *loc. cit.*

† Harned, *loc. cit.*

‡ Hodge, Handbook of Chemistry and Physics.

In the few cases, where available, the literature data compare well with the calculated values. The others are amenable to verification by comparison with the data obtainable by other methods.

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COMPOSITION AND APPARENT INSTABILITY CONSTANT OF URANYL 1-HYDROXY-2-NAPHTHOATE CHELATE

By S. C. Tripathi* and Satya Prakash

The complex formation of uranyl with monosodium 1-hydroxy-2-naphthoate as a chelating agent has been studied and its composition determined by Job's method of continuous variation. The complex is formed at *p*H 4.8 and contains uranyl and 1-hydroxy-2-naphthoate in 1 : 1 ratio, the colour of the complex being deep red. It has been suggested that in the complex formation, the hydroxyl hydrogen of the naphthoate is displaced and oxygen atoms of carboxyl and hydroxyl groups share to form the complex.

Hydroxynaphthoic acids have been found to yield many characterised complexes with various metals in which oxygen atoms of hydroxyl and carboxyl groups take part. Ioffe and coworkers (*J. Gen. Chem. U.S.S.R.*, 1936, **6**, 1006) have investigated iron complexes of 2-naphthol-3- carboxylic acid and have reported the formation of two complexes.

Some simple and complex salts of 3-hydroxy-2-naphthoic acid have been investigated by Margareta and Ceranatescu (*Ann. Sci. Univ.*, Jassy, 1948, **30**, 219).

Kazuoshibata *et al.* (*J. Chem. Soc.*, 1925, 2121) studied iron complex of 2-hydroxy-3 naphthoic acid. The present authors (*Vijnana Parishad Anusandhan Patrika*, 1958, **1**, 1) investigated the uranyl complex with 1-hydroxy-2-naphthoic acid potentiometrically and conductometrically. They have shown that the compound formed is a non-electrolyte.

Experimental

Standard solutions of uranyl nitrate were prepared by direct weighing of the Baker's analysed sample of uranyl nitrate [$UO_2(NO_3)_2.6H_2O$]. Uranium content was estimated gravimetrically (Vogel, "Text-book of Quantitative Inorganic Analysis", London, 1951, p. 471).

For the preparation of monosodium 1-hydroxy-2-naphthoate, the same procedure was adopted as of mono sodium *o*-cresotate (Tripathi and Prakash, this *Journal*, 1958, **35**, 119). 1-Hydroxy-2-naphthoate was prepared by direct weighing of the prepared sample†.

All the measurements were made at 30° ± 0.1°. *p*H was measured by a battery-operated *p*H meter using glass and saturated calomel electrodes. The instrument was standardised with a standard buffer solution.

Colorimetric measurements were made as described previously (Tripathi and Prakash, *loc. cit.*) within transmission range of 500 560 mμ.

Complex-forming Systems.—Several sets of mixtures containing uranyl nitrate and monosodium 1-hydroxy-2-naphthoate in the ratios of 1 : 1, 1 : 2 and 1 : 3 were prepared, as described previously (*loc cit.*).

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† Carbon, hydrogen and oxygen contents were determined by combustion.

To study the composition of the complex by Job's method of continuous variation, different mixtures of uranyl and monosodium 1-hydroxy-2-naphthoate were prepared in various ratios (0.1 – 1.0) of the concentration of the naphthoate to the total concentration of the naphthoate and uranyl ion at a constant *p*H of 4.8. The *p*H of the mixtures was raised by alkali. Total volumes of the mixtures were kept constant. Colorimetric measurements of the solutions were made after the attainment of equilibrium.

For colorimetric measurements, solutions, in which turbidity or precipitate had appeared, were centrifuged to get clear solutions.

Discussion

In the graph the abscissa represents the *p*H or the ratio of the concentrations of monosodium 1-hydroxy-2-naphthoate to the total concentration of the naphthoate and uranyl ion, while the ordinate represents the colorimeter readings.

Fig. 1

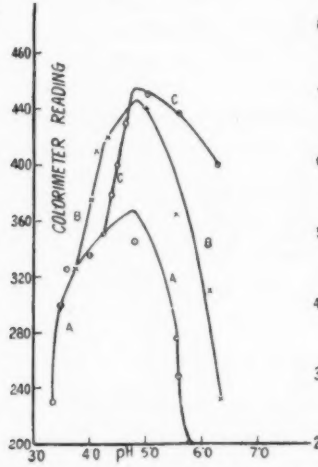


Fig. 3

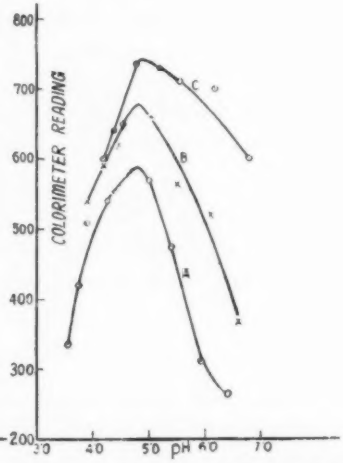


Fig. 1 shows the changes in colour with rise in *p*H by the addition of alkali in 1 : 1, 1 : 2 and 1 : 3 mixtures of 0.0333*M* uranyl nitrate and 0.0333*M* monosodium 1-hydroxy-2-naphthoate. Colorimeter readings are plotted against *p*H (Fig. 1).

In the reddish mixture of uranyl nitrate and the naphthoate, when caustic soda was added, the precipitate obtained by mixing the two reactants dissolved at about *p*H 4.8, the colour of the mixtures being deep red. After a certain *p*H, the colorimeter readings decreased, followed by the precipitation of uranyl hydroxide. In Fig. 1 the curves A-C represent respectively 1 : 1, 1 : 2 and 1 : 3 mixtures. All the curves show that the red colour of the complex increases up to *p*H 4.8, maximum being at the same *p*H (4.8) when an equivalent of alkali has been added. Above this *p*H the dissociation of the complex took place with the decolorisation of the deep red colour, and finally the precipitation of uranyl hydroxide occurred. As the maximum colorimeter reading lies more or less at the same *p*H and by the addition of an equivalent of alkali in all the cases, it shows that only one complex is formed in the systems at *p*H 4.8, and that may be in 1 : 1 ratio of uranyl ion and the naphthoate.

To determine the composition of the complex, Job's method of continuous variation was employed. 0.0333*M*-Uranyl nitrate and 0.0333*M* monosodium 1-hydroxy-2-naphthoate solutions were mixed in various ratios (0.1 to 1.0) of the concentration of the naphthoate to the total concentration of the naphthoate and uranyl nitrate. With the help of *p*H meter, *p*H of each mixture was raised to 4.8 and the total volume to 50 c.c. (Fig. 2). Colorimetric readings, when plotted against the ratios of concentrations of naphthoate to the total concentration of naphthoate and uranyl ion, show maximum at the ratio of 0.5, indicating the formation of 1 : 1 complex. This proves that the complex formed in the systems contains uranyl ion and the naphthoate in 1 : 1 ratio.

On the basis of the above observations of colorimeteric studies, it can be inferred that in the complex formation hydroxyl hydrogen of the naphthoate is displaced and the complex formation takes place with the oxygen atoms of hydroxyl and carboxyl groups. The reaction of the formation of the complex can be represented by

$$UO_2^{2+} + C_{10}H_6\begin{matrix}OH\\COONa\end{matrix} \rightarrow C_{10}H_6\begin{matrix}O\\COO\end{matrix}UO_2 + H^+ + Na^+ \quad \ldots (1)$$

The study of the uranyl complex of *o*-cresotate with Job's method (Tripathi and Prakash, *Z. physikal. Chem.*, under publication), also reveals the formation of a complex containing uranyl ion and *o*-cresotate in 1 : 1 ratio.

In Fig. 3, the curves are of similar nature as the curves of Fig. 1. Fig. 3 shows the changes in colour with rise in *p*H in different mixtures (1 : 1, 1 : 2, and 1 : 3) of 0.025 *M* uranyl nitrate and 0.025 *M* monosodium 1-hydroxy-2-naphthoate. Colorimeter readings, when plotted against *p*H, show maximum at *p*H 4.8, indicating the only one complex as in Fig. 1.

FIG. 2

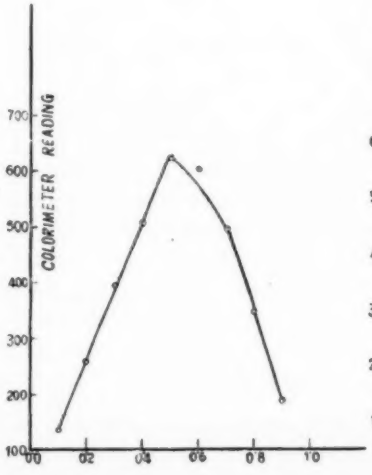
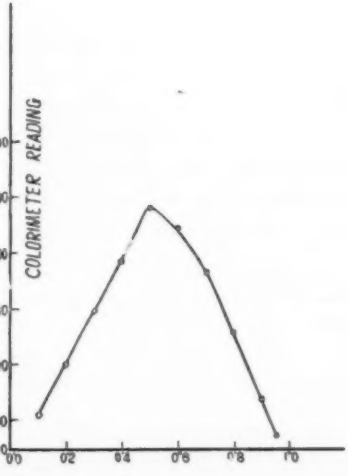


FIG. 4



Naphthoate/naphthoate + UO_2^{2+}.

Fig. 4 shows the study of Job's method at a constant *p*H of 4.8 with one lower concentration (0.025 *M*) of the reactants under similar conditions, as in Fig. 2. Colorimeter readings, on being plotted against the ratios of the concentration of the naphthoate to the total concentration of the naphthoate and uranyl ion, gave maximum at the same ratio 0.5 showing the indication of the same 1 : 1 complex.

The apparent instability constant (K) has been calculated from the data plotted in Figs. 2 and 4. It has already been pointed out that uranyl ion does not show any reading on colorimeter scale with filter Ks 54 within the transmission range of 500-560 mμ and the chelating agent is itself colorless, so the complex is the only coloured substance present in the system and therefore the intensities of the coloured solutions are proportional to the concentrations of the complex formed in the system. Hence, the maxima in the curves show the composition of the complex corresponding to the formula. It would be clear now that in both ascending and descending portions of the curves of Figs. 2 and 4, the same amount of the complex will be formed in every case at constant intensity (colorimeter reading). For example, at 300 colorimeter reading, the same amount of complex will be formed on each side of the curves (ascending as well as descending) in both the Figures 2 and 4.

The apparent instability constant (K) by this method has been calculated by Mukherji and Dey (this *Journal*, 1957, **34**, 465)

$$K = \frac{x}{(a-x)\ (b-x)}$$

where x is the concentration of the complex and a and b are the initial concentrations of uranyl nitrate and monosodium 1-hydroxy-2-naphthoate respectively.

Taking two different concentrations a_1 and a_2, and b_1 and b_2 of the two reactants, uranyl nitrate and the naphthoate, at the same colorimeter reading, *i.e.*, at the same concentration (x) of the complex, we have :

$$K = \frac{x}{(a_1-x)\ (b_1-x)} = \frac{x}{(a_2-x)\ (b_2-x)}$$

$$x = \frac{a_1b_1-a_2b_2}{(a_1-b_1)-(a_2-b_2)}$$

By finding out the value of x by the above equation, K has been calculated at various colorimeter readings, e.g., 290 and 350 in both ascending and descending sides of the curves of Figs. 2 and 4. The average value of K comes out to be $2.42 \pm 0.5 \times 10^{-2}$.

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STUDIES ON THE CATAPHORETIC VELOCITY OF COLLOIDAL PARTICLES BY THE BOUNDARY METHOD. PART I. CHARACTERISTIC CHANGES IN THE VELOCITY OF THE BOUNDARY BETWEEN FERRIC HYDROXIDE SOL AND KCl SOLUTIONS OF DIFFERENT CONDUCTIVITIES AS SUPERNATANT LAYERS

By P. D. Bhatnagar and Abani K. Bhattacharya

Cataphoretic velocity of ferric hydroxide sol has been determined under different voltages by taking different concentrations of KCl as the supernatant layer for the boundary movement in a U-tube. The velocity has also been determined by reversing the current. The cataphoretic velocity-time curves show three distinct stages : a rise in velocity in the initial stage, followed by a practically constant rate of migration in the middle, and then again a rise.

The velocity is slightly reduced by reversing the current, but the formation of a sharp boundary does not take place when the current is reversed again. These results are of importance in the study of the cataphoretic velocity of colloidal particles and throw some light on the complications that should be resolved to obtain correct values of zeta-potential.

Cataphoretic velocity of colloidal particles has been studied by many workers with wide discrepancies in their derived results. Svedberg (*Nov. Act. Reg. Sci.*, Uppsala, 1907, IV-2, 1,147, 190), Burton (*Phil. Mag.*, 1906, *vi*, **11**, 436), Rolla (*Atti Accad. Lincii*, 1908, **17**, 650), Whiteney and Blake (*J. Amer. Chem Soc.*, 1904, **26**, 1339) and Galecki (*Z. anorg. Chem.*, 1912, **74**, 174) obtained different values of c. v. of particles of platinum and gold hydrosols. The foregoing authors as well as J. N. Mukherjee (this *Journal*, 1936, **13**, 372) observed that the method of preparation also affected the migration velocity of the particles. Mayor and Salles (*Compt. rend.*, 1908, **146**, 826) reported that the velocity of the receding boundary of As_2S_3 sol was greater than that in the ascending limb, under direct and reverse currents.

J. N. Mukherjee (*loc. cit.*) attempted to elucidate the interionic repulsions between the mobile ions and the effect of aggregation on the distribution of ions in the double layer, the special role of the adsorption of ions, and the contribution of the colloidal particles to the ionic strength of the medium. He obtained many interesting and characteristic results on the c.v. of the colloidal particles during the process of slow coagulation. In some cases, the c.v. of the aggregates increased and in other cases a diminution and sudden fall near the point of precipitation were observed. On the basis of such observations they critically examined the existing theories and dicussed the relationship between the c.v. and the size and shape of the particles.

Ghosh (*J. Chem. Soc.*, 1929, 2693) observed the influence of organic substances on the c. v. On the basis of their observations it was suggested that the stability of a colloidal solution was not a simple function of the electrical charge but also

depended upon several other factors such as hydration and the tenacity with which the charges were held by the colloidal particles.

It follows from the foregoing ovservations that the systems studied by them are too complicated to be explained, unless much simpler systems are studied in comprehensive detail.

The pure sol by itself exhibits many fluctuations in the rates of its boundary movement with time under a constant voltage. Hence, it is deemed necessary in the first instance to develop a thorough understanding of the characteristic changes in the c.v. of colloidal particles of a pure sol without adding any electrolyte, so that many unknown, yet probable factors which may play their respective roles during the process of slow coagulation, may be eliminated or minimised.

The effect of current reversal on the migration of particles in the opposite direction does not also seem to have received adequate attention.

In view of the foregoing reasons, we have performed some experiments with rigorous care on the c.v. of the particles of dialysed ferric hydroxide sol, both in the field of direct and reverse currents by the moving boundary method, the results of which have been presented and discussed in this paper.

EXPERIMENTAL

The sample of $Fe(OH)_3$ sol was prepared by adding concentrated ammonium carbonate solution to a 5% solution of ferric chloride with constant stirring until the precipitate just ceased to dissolve. The precipitated ferric hydroxide was then peptised by adding just the quantity of 5% ferric chloride solution. The mixture was then dialysed in a parchment paper bag against running distilled water till the dialysate was completely free of ferric iron and almost free of the chloride ions. The complete absence of ferric iron in the dialysate indicates complete absence of free ferric chloride.

Estimation.—The sol (25 c.c.) was dissolved in the requisite quantity of HCl (conc.). The excess of HCl was boiled off and the solution was then reduced by granulated zinc in presence of H_2SO_4. Iron was then estimated against a standard solution of $KMnO_4$.

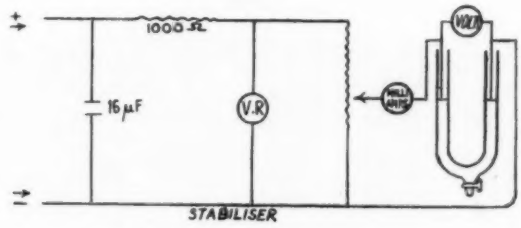
The cataphoretic velocity (c.v.) was observed in a U-tube by Burton's method in which migration of the boundary between the sol and the supernatant liquid was measured accurately with the help of a cathetometer under an illuminated background. The sol was very slowly entered through the stoppered jet of the U-tube to form a sharp boundary, taking special care to minimise diffusion. The inlet pressure was regulated by two stoppers to allow the stream of the sol to a second U-tube very slowly. The experiments were performed under thermostatic control at $25° \pm 0.2°$.

In order to determine the length of the U-tube, the total resistance of 0.1 *N*-KCl column covering the electrodes in the U-tube was first determined. The resistance offered by 1 cm height was obtained by withdrawing 1 cm column of the liquid from the U-tube. The mean of several readings was taken to determine the resistance/cm of the column. Then, total resistance divided by resistance/cm, gave the correct length, and voltage/length gave the potential gradient.

The constant voltage supply was obtained from the Heayberd rectifier unit which had been fitted with a voltage stabilising tube (V.R. 105 : JAN, CHY-OC_3, V. T. 200

HYTRON.) in the circuit. The arrangement of the voltage control is shown by the following circuit diagram.

FIG 1



The desired stabilised voltage was tapped by means of a variable resistance. A voltmeter in parallel and a milli-ammeter in series were used during the measurement of c.v. (no fluctuation of voltage or current was observed).

Concentration of $Fe(OH)_3$/litre of the sol = 12.39 g. Conductivity of the sol = 2.4×10^{-4} mhos at 30°.

OBSERVATIONS

The important observations worthy of note were the following :-

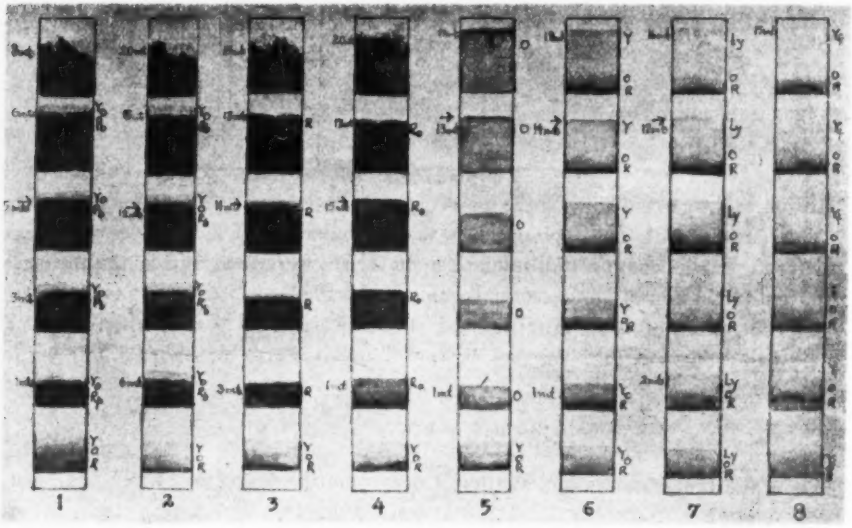
(*a*). The appearance of the boundary before passing the current, as seen through the cathetometer, clearly indicated that the boundary was less sharp having a light yellow colour at the top, the intensity of which deepened into the sharp reddish colour of the sol just below. This was probably due to the unavoidable effect of diffusion in spite of the utmost care taken to form the boundary (Fig. 2, Plates 1, 2.....8 ; the bottom portions).

(*b*). When the migration of the particles was observed by taking the supernatant liquid (KCl) of the same conductivity as that of the sol, the yellow layer of the boundary became sharper within a few minutes of passing the current. Gradually the yellolw layer vanished and the sharpest boundary was formed having the red colour of the sol itself. This observation is very characteristic and is easily reproducible. It appears from this that the red particles move faster than the yellow ones and overtake them in a short time to bring about the conditions of forming a sharp boundary that moves with a steady velocity (Plate 4). The migration velocity of particles was slower to start with, till the sharp boundary was formed during which the velocity slightly increased, and then remained practically constant for a certain period. Then this boundary assumed the appearance of a more compact profile of thin layers between which transitory pointed shaped formations were visible in the cathetometer. During this period the c.v. slightly increased, due probably to temporary temperature effect caused by the time lag of adjustment with the thermostat.

(*c*). If the current were passed for a longer time after this stage, the boundary became ruffled and uneven, so that the cross wire of the microscope could not

get any plane surface to coincide with. This effect might be due to the disturbance created by local convection currents set up inside the tube in spite of the thermostatic control outside the U-tube (Plates 1, 2, 3 and 4, top portions).

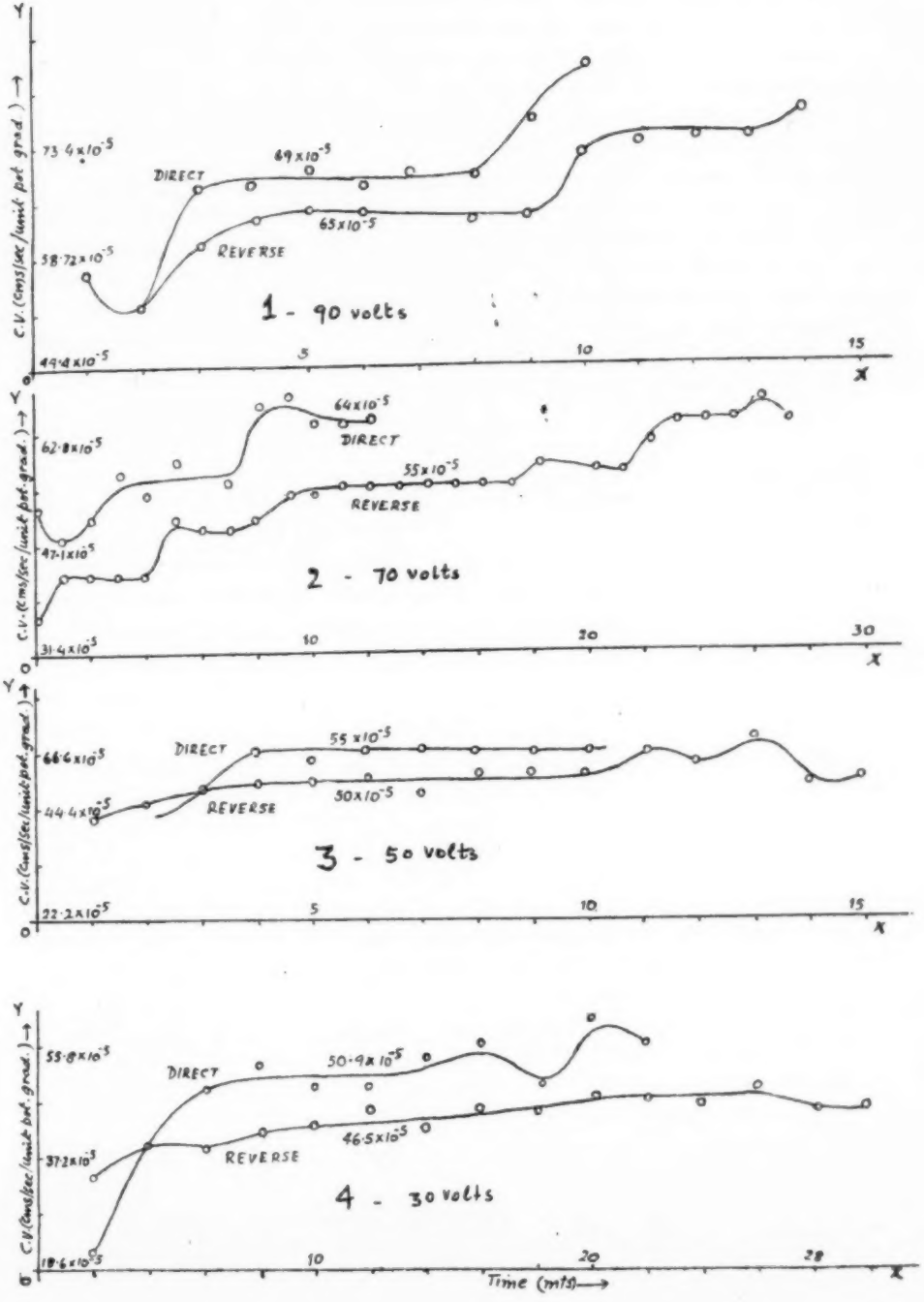
FIG. 2



	Conductivity of the supernatant liquid.	
Y_f-Yellow faint.	Plate No. 1:	8.1×10^{-4} mhos.
L_y-Yellow light.	Plate No. 2:	4.58×10^{-4}
Y -Yellow.	Plate No. 3:	3.18×10^{-4}
O -Orange.	Plate No. 4:	2.4×10^{-4}
R -Red.	Plate No. 5:	1.66×10^{-4}
R_b-Reddish brown.	Plate No. 6:	1.16×10^{-4}
P_b-Purple brown.	Plate No. 7:	0.42×10^{-4}
	Plate No. 8:	0.21×10^{-4}

(*d*). The yellow layer in the opposite limb was elongated as the particles of the red boundary moved downwards in this column. When the current was reversed, it took much longer time for the formation of a sharp boundary in this limb than that required for the direct current in the other limb of the U-tube. The c.v. by reversing the current was found to be slightly less (about 8 to 10%) than the initial velocity observed with direct current (Fig. 3, curves 1, 2, 3 and 4).

FIG. 3


Y
C.V. (Cms/sec/unit pot. grad.) →
73.4x10⁻⁵
DIRECT
69x10⁻⁵
65x10⁻⁵
REVERSE
58.72x10⁻⁵
1 - 90 volts
49.8x10⁻⁵
5
10
15
X
64x10⁻⁵
DIRECT
62.8x10⁻⁵
55x10⁻⁵
REVERSE
47.1x10⁻⁵
2 - 70 volts
31.4x10⁻⁵
10
20
30
66.6x10⁻⁵
DIRECT
55x10⁻⁵
REVERSE
50x10⁻⁵
44.4x10⁻⁵
3 - 50 volts
22.2x10⁻⁵
55.8x10⁻⁵
DIRECT
50.9x10⁻⁵
46.5x10⁻⁵
37.2x10⁻⁵
REVERSE
4 - 30 volts
18.6x10⁻⁵
Time (mts) →

(*e*). *Effect of Voltage.*—From Table I it is observed that the compact layer formation, as described under (*b*), takes place at greater distances from the starting point (*i. e.* nearer the opposite electrode) as the applied voltage is increased. This is due to the greater velocity of the boundary layer under higher potential gradient.

The velocity-time curves of the moving boundary at four different voltages (30, 50, 70 and 90 volts) with an equiconducting solution of KCl as upper liquid show three specific changes (Fig. 3, curves 1-4). In the earlier stage, the velocity of the particles usually shows a steep rise and then it becomes steady for a certain interval, followed later on by a similar rise. These curves in the beginning and in the ending intervals resemble in some cases the S-shaped (autocatalytic) curves which are obtained in the case of certain reaction rates and in the rate of slow coagulation observed by measuring the variations of such physical properties as viscosity or light extinction. It is, however, difficult to determine or define at this preliminary stage of our investigations what actually takes place with the migrating particles in the electric field when we measure the c.v. by boundary movement.

TABLE I

Boundary position before passing current.	Final position for compact layer formation.	Distance moved.	Time.	Distance of compact layer from the electrode (cm).
	90 Volts.			
1. 1.882	2.874	0.994 cm.	12 mins.	11.75 − 2.87 = 8.88
2. 1.748	2.910	1.160	13	11.75 − 2.91 = 8.84
3. 1.418	2.582	0.964	14	11.73 − 2.58 = 9.15
4. 1.484	2.680	1.000	13	11.78 − 2.68 = 9.10
5. 1.648	2.660	1.012	13	11.77 − 2.66 = 9.11
6. 1.540	2.450	1.110	12	11.40 − 2.44 = 8.95
		Mean 1.055		Mean = 8.97
	70 Volts.			
1. 1.400	2.350	0.950	13	11.65 − 2.44 = 9.21
2. 1.370	2.360	0.990	15	11.68 − 2.36 = 9.32
3. 1.300	2.250	0.950	13	11.64 − 2.25 = 9.39
4. 1.250	2.340	0.990	12	11.66 − 2.34 = 9 32
		Mean 0.970		Mean = 9.31
	50 Volts.			
1. 1.450	2.230	0.780	20	11 82 − 2.23 = 9.59
2. 1.450	2.290	0.840	18	11.78 − 2.30 = 9.48
3. 1.410	2.220	0.810	17	11.68 − 2.23 = 9 45
		Mean 0.810		Mean = 9.50
	30 Volts.			
1. 1.464	2.142	0 668	24	11.70 − 2.15 = 9.55
2. 1.255	1.920	0.664	22	11.50 − 1.92 = 9.57
3. 1.350	1.970	0.620	24	11.60 − 1.97 = 9.63
		Mean 0.664		Mean = 9.58

It is interesting to note that by reversing the current again, the sharp boundary layer is not formed. From this it may be inferred that the double layer, which is the main basis of the stability of the sol, is gradually destroyed by alternating the field of migration.

(f) Effect of changing the concentration of the supernatant electrolyte (KCl *solution*) *at constant voltage* (70 volts).—When the migration of the boundary was observed with pure conductivity water as the supernatant liquid, very faint yellow boundary layer moved and broadened out gradually as the current was passed. The red boundary below the yellow layer did not move with any appreciable speed. This suggests that the yellow layer is made of colloidal particles of very fine dimensions capable of moving in aqueous layer under the electrical field.

The changes brought about in the migration of the yellow layer by very gradually increasing the conductivity of the supernatant electrolyte to approach the concentration of the equiconducting solution are expressed in Plates 7, 6 and 5 (Fig. 2) and those brought about by the supernatant electrolyte of higher conductivity (up to four times that of the sol) are shown in Plates 3, 2 and 1 (Fig. 2).

It will be seen from the legend of these plates that the yellow layer is gradually replaced by orange and finally by red, when the conductivity of the supernatant liquid is gradually raised to that of the sol.

The best results were, however, obtained for the formation of a sharp boundary of red colour corresponding to that of the sol, when the conductivity of the supernatant liquid was equal to that of the sol. This important condition for determining the c.v. was also observed and recommended by Mukherjee *et al.* (*loc. cit.*), Ghosh and others (*loc. cit.*).

Discussion

The foregoing observations are significant to suggest that the sol is composed of particles of different size and shape and, hence, of different charge density and boundary potentials. On account of this the yellow and red boundaries move with different speeds in the electric field, one being faster or slower than the other according to the conditions of the system. These boundaries, however, could merge together forming a sharp layer when the conductivity of the electrolyte used as supernatant liquid was equal to that of the sol. When pure conductivity water was taken as the supernatant liquid, it was rather a unique observation that only the faint yellow layer moved, but the red boundary remained almost stationary, and the two did not merge into a sharp boundary as had been observed when equiconducting supernatant electrolyte was taken. When the concentration of the supernatant electrolyte exceeded that of the equiconducting solution, the yellow and red boundaries came nearer, and continued to exist as separate layers closer to each other, in spite of their movements under the applied potential gradient (Fig. 2, Plates 1, 2 and 3). More detailed investigations may furnish relevant data to explain these observations.

The influence of the supernatant electrolytes of less conductivity than the sol (water being the limiting case) seems to throw an interesting light on the character and types

of $Fe(OH)_3$ micelles that were formed when the sol was prepared by the ammonium carbonate method. The gradual changes of colour (yellow faint → yellow light → yellow → orange → red → dark red) of the moving boundary layers, as the concentration of the supernatant electrolyte is changed from zero onwards, give a strong evidence for the heterogeneous composition of the system as a whole, depending upon the size, shape, hydration and double layer characteristics of the particles present.

In the light of the above observations the immense complexities that shall have to to be resolved in order to determine the c. v. of colloidal particles can be easily foreseen. Without resolving such complexities of the system the values of ξ-potential cannot be standardised even with the same sol, and this difficulty has been experienced by many eminent workers in this field.

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STUDIES IN CARBOHYDRATES. PART IX STRUCTURE OF THE DEGRADED GUM FROM *ACACIA CATECHU*

By R. K. Hulyalkar, T. R. Ingle and B. V. Bhide

The degraded gum, obtained by autohydrolysis, has been found to be composed of D-galactose and D-glucuronic acid only in the proportion of 4 : 1 respectively. On methylation and hydrolysis, it yields (1) 2 : 3 : 4 : 6-tetra- (1 mol.), (2) 2 : 3 : 4-tri- (1 mol.), (3) 4 : 6-di-*O* methyl-D-galactopyranose (2 mol.) and (4) 2 : 3 : 4-tri-*O*-methyl-D-glucopyranosyl-uronic acid (1 mol.). On the basis of these results, a probable structure to the repeating unit of the degraded gum has been proposed.

The composition of the gum from *Acacia catechu* (generally known as Khair gum in the Bombay State) and the identification of its resistant part have been already published (this *Journal*, 1956, **33**, 861). The present work deals with the structure of the degarded gum obtained by autohydrolysis of the total gum.

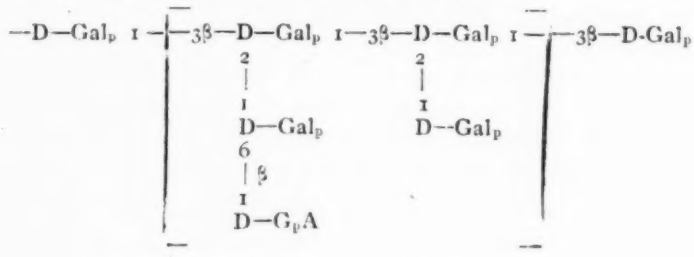
The hydrolysate of the gum, obtained by heating the aqueous gum solution at 90° for 40 hours, yielded the degraded gum as a white powder. It contained D-galactose and D-glucuronic acid only, in the proportion of 4 : 1 repectively. Hydrolysis of the degraded gum by 10% sulphuric acid yielded an aldobiouronic acid, which was found to be 6-β-*O*-(D-glucopyranosyl-uronic acid)-D-galactopyranose, identical to the resistant part obtained from the total gum.

On methylation and hydrolysis, the degraded gum yielded (1) 2 : 3 : 4 : 6-tetra-, (2) 2 : 3 : 4 tri-, (3) 4 : 6-di-*O*-methyl-D-galactopyranoses and (4) 2 : 3: 4-tri-*O*-glucopyranosyl-uronic acid, as different methylated sugars. All these sugars were characterised by (*i*) comparing their physical properties and R_f values with authentic samples as well as (*ii*) by preparing their crystalline derivatives. The yields of different sugars obtained from cellulose column indicate that they are present in the methylated degraded gum in the proportion of 1 : 1 : 2 : 1 respectively.

From the above results, the following information can be obtained about the structure of the gum As L-arabinose is completely removed in autohydrolysis, it appears to be present in the total gum in the furanose form. The repeating unit of the degraded gum appears to be composed of four units of D-galactose and one unit of D-glucuronic acid (calc. equiv. 842 ; found 850). The identification of 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid as the only derivative of uronic acid indicates that D-glucuronic acid is present in the degraded gum, only as the end-group. In view of the facts that (*i*) no other derivative of D-galactose possessing -OH group on C_6 has been obtained except 2 : 3 : 4 tri-*O*-methyl-D-galactoypranose, (*ii*) 2 : 3:4 tri-*O*-methyl-D-galatopyranose and 2 : 3 : 4 tri-*O*-methyl-D-glucuronic acid are present in the methylated degraded gum in equal proportions and (*iii*) 6-β-*O*-(D-glucopyranosyl-uronic acid)-D-galactopyranose has been found to be the resistant part of the degraded gum, it appears that the

aldobiouronic acid is present as one of the branches of the gum attached to the skele to n. The isolation of one unit of 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactopyranose indicates the other branch in the repeating unit. The remaining two D-galactose units appear in the hydrolysate as 4 : 6-di-*O*-methyl-D-galactopyranose, suggesting that the skeleton of the gum consists of D galactose units linked either through 1 : 2 linkage or 1 : 3 linkage or both. The low optical rotations of the degraded gum and its methylated product indicate β-linkages.

Several different structures can be suggested for the degraded gum. Gum arabic, however, is known to contain a skeleton of 1 : 3-linked D-galactopyranose units (Dillon *et. al.*, *Proc. Roy. Irish Acad.*, 1953, **55B**, 331 ; 1954, **57B**, 31). Assuming that similar skeleton is present in this gum also, the repeating unit of the degraded gum under investigation appears to be of the following type :



EXPERIMENTAL

Isolation of the Degraded Gum.—The gum (25 g.), dissolved in water and made up to 500 c.c., was heated on a water-bath at 90° for 40 hours. The hydrolysis was followed by the determination of optical rotation and the reducing power of the hydrolysate.

TABLE I

Hours ...	5	10	15	20	25	30	40
$[\alpha]_D^{28}$ ...	−6°	+ 4°	+ 17°.6	+ 28°	+ 33°	+ 39°	+ 40°.9
% Reducing sugar (in terms of glucose) ...	9.3	19.1	25.9	33.5	35	38	39.5

After 40 hours, the hydrolysate was concentrated under reduced pressure to a small volume (100 c.c.) and added to alcohol (200 c.c.), when the degraded gum separated as a flocculent white precipitate. Monosaccharides were removed by washing the precipitate repeatedly by ethanol-water mixture (70 : 30).

The degraded gum was acidic to litmus and it reduced Fehling's solution. It had equiv. 850, $[\alpha]_D^{28}$ 0° (*c*, 1 in water) and uronic anhydride, 21.6%. On hydrolysis with 10% H_2SO_4, it yielded galactose as a non-acidic reducing sugar. The resistant part obtained in this hydrolysis was found to be 6-β-(D-glucopyranosyl-uronic acid)-D-galactopyranose by methylation and hydrolysis, as described before (*loc. cit.*).

The analysis of the degraded gum indicates that it is composed of D-galactose and D glucuronic acid in the proportion 4 : 1 respectively, which requires equiv. wt., 842, uronic anhydride, 24.6%.

Methylation of the Degraded Gum.—The degraded gum (8.5 g.) was methylated five times by dimethyl sulphate and sodium hydroxide, and finally twice by Purdie's reagent. It was isolated as a semisolid in 6.8 g. yield; OMe, 42.8%, $[\alpha]_D^{28}$ -48°.2. It was dissolved in chloroform (50 c.c.) and fractionally precipitated by adding petroleum ether (b.p. 60-80°, 50 c.c. each time).

TABLE II

Fractions.	Yield.	$[\alpha]_D^{28}$ (c = 1 in $CHCl_3$).	%OMe.
I	1.1 g.		39.1
II	2.5	−45°.2	42.5
III	1.5	−48°	43.8
IV	1.5	−48°	43.8

Methanolysis and Hydrolysis of Fractions III *and* IV.—Fractions III and IV (3 g.) were dissolved in methanolic HCl (7%, 120 c.c.) and heated to 110° in sealed tubes for 12 hours. The solution was cooled, neutralised with silver carbonate and hydrogen sulphide was passed to remove Ag^+ ions. The filtrate on concentration under reduced pressure was treated with barium hydroxide (0.33 *N*, 25 c.c.) for 3 hours at 55°. Barium hydroxide was neutralised with CO_2, filtered and the filtrate was evaporated to dryness. On extraction with dry ether, non-acidic reducing sugars were obtained as a syrup (A) (2.1 g.) while the acidic sugars remained as their barium salts as a residue (B) (0.7 g).

Syrup (A).—The syrup on keeping deposited crystals, which were removed by triturating with ether and filtering from the mother-liquor. On crystallisation from ether-acetone mixture, it had m.p. 161-62°, indicating that it might be β-methyl-4 : 6-di-*O*-methyl-D-galactactopyranoside (0.2 g.). The mixed m. p. with the authentic specimen remained unchanged. It was further confirmed by hydrolysing and preparing its anilide, m.p. and mixed m.p. 206°.

Isolation and Identification of Different Sugars from Cellulose Column

The sugar syrup obtained after filtration of crystals was heated with 1*N*-H_2SO_4 (25 c.c.) for 3 hours at 90° and worked up in the usual manner to obtain reducing methylated sugars (yield 1.8 g.). The chromatographic examination indicated the presence of three sugars which were identified as (1) 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactopyranose, (2) 2 : 3 : 4-tri-*O*-methyl-D-galactopyranose and (3) 4 : 6-di-*O*-methyl-D-galactopyranose by running authentic samples side by side. The sugar syrup (1.7 g.) was poured on the top of the cellulose column (4 × 46 cm) and different sugars were eluted by using benzene : ethanol : water (169 : 47 : 15 v/v) as an eluting solvent. The fractions were collected in 10 c.c. portions and those indicating one type of sugar were grouped together and evaporated to a syrup.

2 : 3 : 4 : 6-*Tetra*-O-*methyl*-D-*galactopyranose.*—Fraction (I), yield 0.43 g., OMe 52.5%, $[\alpha]_D^{28}$ + 115° (*c*, 0.55 in water) was found to be 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactose on a chromatogram, using the authentic sample. It was confirmed by preparing its anilde ; m.p. and mixed m.p. 193°.

2 : 3 : 4-*Tri*-O-*methyl*-D-*galactopyranose*.—Fraction (II), yield 0.43 g., OMe 38.8%, indicated the presence of 2 : 3 : 4-tri-*O*-methyl-D-galactose, which was confirmed by a chromatogram with the authentic sample. The syrup crystallised on addition of water (1 or 2 drops). On crystallisation from acetone-ether, it melted at 78°. It gave an anilde ; m.p. and mixed m.p. 165°.

4 : 6-*Di*-O-*methyl*-D-*galactopyranose*.—Fraction (III), yield 0.75 g., from the chromatographic examination and methoxyl content (26.8%) was found to be 4 : 6-di-*O*-methyl-D galactopyranose. It crystallised from water, m.p. and mixed m.p. 104°. It yielded an anilide ; m.p. and mixed m.p. 206°, $[\alpha]_D^{28}$ −169° (*c*, 0.33 in pyridine) (cf. Hirst and Jones, *J. Chem. Soc.*, 1939, 1488). It gave an osazone, m.p. and mixed m.p. 151°.

Examination of Residue (*B*) (yield 0.70 g.) : *Identification of* 2 : 3 : 4-*Tri*-O-*methyl*-D-*glucuronic Acid*.—The barium salt (0.7 g.) was heated with methanolic-HCl (3%, 10 c.c.) for 8 hours on a water-bath at 90°. The solution was neutralised with Ag_2CO_3, filtered, concentrated and distilled. It gave an ester, b.p. 130-40°/1 mm, OMe 58.2, $[\alpha]_D^{28}$ + 80° (*c*, 0.33 in water), n_D^{28} 1.4496. On treatment with methanolic ammonia at 0°, it gave an amide, m.p. and mixed m.p. 186°, $[\alpha]_D^{28}$ + 136° (*c*, 0.5 in water).

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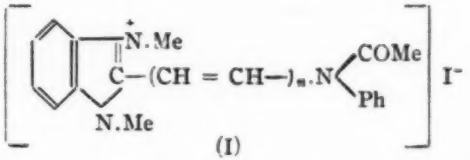
MEROCYANINES DERIVED FROM BENZIMIDAZOLE

By Prabhat Kumar Misra Birendra K. Patnaik and M K. Rout

2-Methyl-*N*-methylbenzimidazole methiodide has been treated separately with diphenylformamidine, β-anilinoacrolein anil hydrochloride and glutaconic aldehyde dianilide hydrochloride. The resulting acetanilido vinylogous compounds have been finally condensed with different thiazolidones, yielding merocarbo-, merodicarbo- and merotricarbo-cyanines and their absorption and photosensitising action studied.

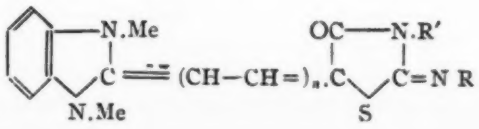
Merocyanines derived from 4-aryl-2-methylthiazoles have been recently reported (Rout *et al.*, this *Journal*, 1958, **35**, 511); the shifts in the absorption maxima between successive vinylene homologues in the above series are now under investigation. Merocyanines containing benzimidazole nucleus do not, however, seem to have been studied before. Merocyanines are constituted of one basic and one acidic nucleus and the variation of the basic component is likely to cause much change in sensitising properties as well as in absorption of the corresponding successive vinylene homologues. It was therefore considered worthwhile to synthesise some merocyanines containing benzimidazole ring.

In the present investigation, 2-methyl-*N*-methylbenzimidazole methiodide was condensed with diphenylformamidine, β-anilinoacrolein anil hydrochloride and glutaconic aldehyde dianilide hydrochloride, yielding acetanilido compounds of type I (n = 1, 2 or 3).



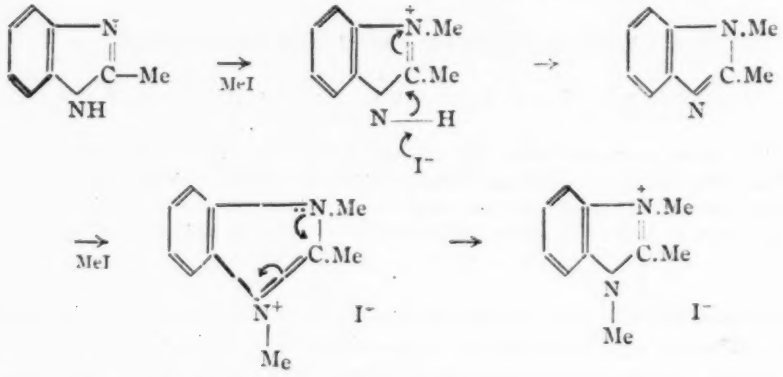
(I)

These intermediate acetanilido compounds (I : n = 1, 2, 3) were subsequently condensed with different thiazolidones which served as the acidic nuclei, the reaction being accomplished in acetic anhydride in presence of fused sodium acetate. The expressions for the final products are indicated below.



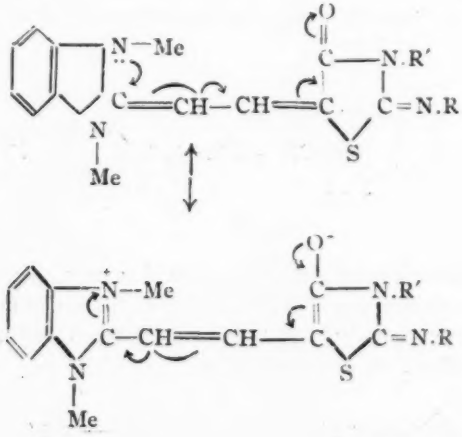
[R = aryl or substituted aryl group ; R' = H or aryl group]

It may be of interest to mention that the reaction of 2-methylbenzimidazole with methyl iodide affords 2-methyl-*N*-methylbenzimidazole methiodide. Methylation of the NH group must have occurred according to the mechanism :

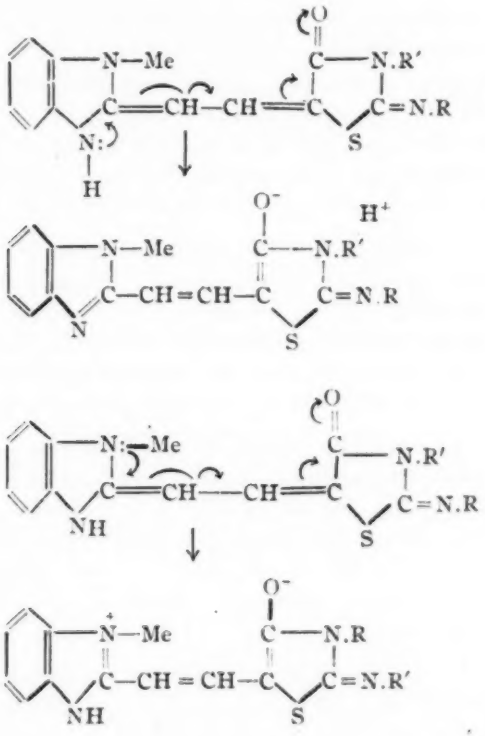


It was fortunate that methylation of NH, which was necessary for increased absorption and photosensitisation, occurred in this way. The effect of NH on increased absorption will be evident from the following discussion.

As is well known, the colour of polymethine dyes is explained by way of the resonance theory, according to which a given compound is regarded as a hybrid or blend of contributing structures, both in the ground and excited states. When applied to the present series of dyes, it will be seen that there will be resonance between the two following structures :



If there is NH group in position-1 instead of N.Me, another possible direction for flow of electrons will be as shown below, and this will naturally oppose fixation of a double bond at positions 2 and 3, which is, however, necessary for increased absorption of the system.



EXPERIMENTL

2-Methylbenzimidazole was prepared by the method of Ladenburg (*Ber.*, 1875, **8**, 677) and its methylation was effected by the method described in Beilstein (4th edition, Band XXIII, p. 145).

β-Anilinoacrolein Anil Hydrochloride.—Trimethoxypropene (4.5 c.c.) and freshly distilled aniline (9 c.c.) were mixed in a 250 c.c. round bottomed flask fitted with water condenser in a reflux position. No reaction was observed at this point except that the mixture turned yellow. On very gradual addition (without shaking) of HCl (conc.) through the condenser, a violent reaction took place. After heating on the steam-bath for 5 minutes, the dark liquid was poured into crushed ice and water in a 400 c.c. beaker whereupon the anil hydrochloride separated as a pale yellow solid. It was filtered, washed very freely with water and then with acetone to remove all the water. The solid darkened slightly in colour, m.p. 208°.

Glutaconic Aldehyde Dianilide Hydrochloride.— 2 : 4-Dinitrophenylpyridinium chloride (3.5 g., prepared by the interaction of 2 : 4-dinitrochlorobenzene and dry pyridine in absolute alcohol) was dissolved in boiling absolute alcohol (21 c.c.) and aniline (3.5 g.) was added slowly down the condenser with shaking, when crystals of dianilide separated. The steam was turned off and HCl (conc., 3.5 c.c.) was added slowly to the reaction mixture and the whole was chilled overnight at about 0°. The product was purified by

stirring it with two or three successive portions of boiling acetone to remove aniline hydrochloride, and filtered hot, m.p. 130°.

2-(2-*Acetanilido-vinyl*)-N-*methylbenzimidazole Methiodide*.—A mixture of 2-methylbenzimidazole methiodide (1.37 g.) and diphenylformamidine (0.98 g.) in acetic anhydride (10 c.c.) was refluxed for 3 hours at 150°. The mixture was cooled, treated repeatedly with ether and crystallised from methanol as needle-shaped crystals, m.p. 170° (decomp.), yield 30%. (Found : C, 52.31 ; H, 4.40. $C_{19}H_{20}ON_3I$ requires C, 52.65 ; H, 4.61%).

2-(4-*Acetanilido*-1 : 3-*butadienyl*)-N-*methylbenzimidazole Methiodide*.—A mixture of 2-methylbenzimidazole methiodide (2.74 g.) and β-anilinoacrolein anil hydrochloride (2.58 g.) in acetic anhydride (15 c.c.) was refluxed for 3 hours at 150°. Excess of acetic anhydride was removed by distillation under reduced pressure. The residue was repeatedly treated with ether and then recrystallised from methanol, m.p. 250°, yield 50%. (Found : C, 54.70 ; H, 4 61. $C_{21}H_{22}ON_3I$ requires C, 54.90 ; H, 4.79%).

2-(6-*Acetanilido*-1 : 3 : 5-*hexatrienyl*)-N-*methylbenzimidazole methiodide* was prepared by refluxing 2-methylbenzimidazole methiodide (2.74 g.) and glutaconic aldehyde dianilide hydrochloride (2.84 g.) in acetic anhydride (15 c.c.) at 150° for 3½ hours. Excess of acetic anhydride was removed by distillation under reduced pressure ; the residue was cooled and thoroughly washed with ether. It was then kept in contact with methanol, m.p. 260° (decomp.), yield 55%. (Found : C, 56.85 ; H, 4.60. $C_{23}H_{24}ON_3I$ requires C, 56.90 ; H, 4.94%).

5-[1 : 3 - *Dimethyl* - 2(3H) - *benzimidazolylidene*) - *ethylidene*] - 2 - *phenylimino* - 4-*thiazolidone* was prepared by refluxing a mixture of 2-phenylimino-4-thiazolidone (0.1 g.) and 2-(2-acetanilidovinyl)-benzimidazole methiodide (0.2 g.) in acetic anhydride (10 c.c.) in presence of fused anhydrous sodium acetate for 3 hours at 170°. The mixture was cooled, water was added and the mixture stirred thoroughly and kept for an hour. It was filtered, washed with water and recrystallised from methanol, m.p. > 300°, yield 50%. (Found : C, 66.07 ; H, 4.62. $C_{20}H_{18}ON_4S$ requires C, 56.29 ; H, 4.97%).

5-[(1 : 3-*Dimethyl*-2(3H)-*benzimidazolylidene*)- *ethylidene*]- 2 - α - *naphthylimino* - 4 - *thiazolidone*.—2-α-Naphthylimino-4-thiazolidone (0.24 g.) and 2-(2-acetanilidovinyl)-benzimidazole methiodide (0.41 g.) in acetic anhydride (10 c.c.) were heated for 3 hours at 160° in presence of anhydrous sodium acetate. The mixture was cooled, treated with water, filtered, washed thoroughly with water and recrystallised from hot methanol, m.p. 113°, yield 40%. (Found : C, 70.85 ; H, 4.74. $C_{24}H_{20}ON_4S$ requires C, 71.28 ; H, 4.94%).

5-[(1 : 3-*Dimethyl*-2(3H)-*benzimidazolylidene*)-*ethylidene*]-2-β-*naphthylimino*- 4 - *thiazolidone* was prepared as above by refluxing 2-β-naphthylimino-4-thiazolidone (0.24 g.) and 2-(acetanilidovinyl)-benzimidazole methiodide (0.41 g.), m. p. 122°, yield 43%. (Found : C, 71.08 ; H, 4.70. $C_{23}H_{18}ON_4S$ requires C, 71.28 ; H, 4.94%).

5-[(1 : 3-*Dimethyl*-2(3H)-*benzimidazolylidene*)-*ethylidene*]-3-*phenyl*-2-*phenylimino*-4-*thiazolidone* was prepared as above by heating 2-(2-acetanilido-vinyl)-benzimidazole methiodide (0.41 g.) and 3-phenyl-2-phenylimino-4-thiazolidone (0.27 g.) for 90 minutes at 170°. After cooling, the product was washed with cold water, followed by acetone to

remove tarry products. It was finally recrystallised from hot methanol, m.p. 150°, yield 38%. (Found : C, 74.10 ; H, 5.03. $C_{26}H_{22}ON_4S$ requires C, 74.64 ; H, 5.26%).

5-[(1 : 3-*Dimethyl*-2(3H)-*benzimidazolylidene*)-*ethylidene*]-3-*o*-*tolyl*-2-*o*-*tolylimino*-4-*thiazolidone* was obtained in a similar way from 3-*o* tolyl-2-*o*-tolylimino-4-thiazolidone (0.6 g.) and 2-(2-acetanilidovinyl)-benzimidazole methiodide (0 82 g.). It was cooled, water was added and kept overnight. It was then filtered and washed with cold water repeatedly and recrystallised from methanol, m.p. 130°, yield 48%. (Found : C, 71.83 ; H, 5.31. $C_{28}H_{26}ON_4S$ requires C, 72.10 ; H, 5.58%).

5-[1 : 3-*Dimethyl*-2(3H)-*benzimidazolylidene*)-*ethylidene*]-3-p-*tolyl*-2-p-*tolylimino*-4-*thiazolidone* was prepared as its *o*-tolyl analogue by refluxing 3-*p*-tolyl-2-*p*-tolylimino-4-thiazolidone (0.29 g.) and 2-(2-acetanilidovinyl)-benzimidazole methiodide (0.1 g.). It was isolated similarly and recrystallised from methanol, m.p. 224° (decomp.), yield 40%. (Found : C, 72.04 ; H, 5.41. $C_{28}H_{26}ON_4S$ requires C, 72.10 ; H, 5.58%).

5-[4-(1 : 3-*Dimethylbenzimidazolin*-2-*ylidene*)-*buten*-1-*ylidene*]-2-*phenylimino*-4-*thiazolidone*.—2-Phenylimino-4-thiazolidone (0.2 g.) and 2-(4-acetanilido-1 : 3 butadienyl)-benzimidazole methiodide (0.45 g.) were heated at 150° for 3 hours in acetic anhydride with fused sodium acetate. It was cooled, water was added and filtered. It was washed repeatedly with water. It was finally recrystallised from methanol, m.p. >300°, yield 55%. (Found : C, 67.89 ; H, 4.89. $C_{22}H_{20}ON_4S$ requires C, 68 04 ; H, 5.15%).

5-[4-(1 : 3-*Dimethylbenzimidazolin*-2-*ylidene*) *buten*-1-*ylidene*]-2-α-*naphthylimino*-4-*thiazolidone* was prepared by heating under reflux 2-α-naphthylimino-4-thiazolidone (0.24 g.) and 2-(4-acetanilido-1 : 3-butadienyl)-benzimidazole methiodide (0.45 g.) in acetic anhydride (10 c.c.) in presence of fused sodium acetate. It was isolated as described above, m.p. >300°, yield 50%. (Found : C, 71.01 ; H, 4.80. $C_{26}H_{22}ON_4S$ requires C, 71.23 ; H, 5.02%).

5-[4-(1 : 3-*Dimethylbenzimidazolin*-2-*ylidene*)-*buten*-1-*ylidene*]-2-β-*naphthylimino*-4-*thiazolidone* was prepared and isolated as above from 2-β-naphthylimino-4-thiazolidone (0.24 g.) and 2-(4-acetanilido-1 : 3-butadienyl)-benzimidazole methiodide (0 45 g.), m.p. 233-37° (decomp.), yield 48%. (Found : C, 70.84 ; H, 4.78. $C_{26}H_{22}ON_4S$ requires C, 71.23 ; H, 5.02%).

5-[4-(1 : 3-*Dimethylbenzimidazolin*-2-*ylidene*)-*buten*-1-*ylidene*]-3-*phenyl*-2-*phenylimino*-4-*thiazolidone* was prepared similarly by refluxing a mixture of 3-phenyl-2-phenylimino-4-thiazolidone (0.27 g.) and 2-(4-acetanilido-1 : 3-butadienyl)-benzimidazole methiodide (0.45 g.) in 8 c.c. of acetic anhydride. It was cooled, washed repeatedly with water and recrystallised from methanol, m.p. >300°, yield 47%. (Found : C, 72.03 ; H, 4.81. $C_{28}H_{24}ON_4S$ requires C, 72.41 ; H, 5.17%).

5-[4-(1 : 3-*Dimethylbenzimidazolin*-2-*ylidene*)-*buten*-1-*ylidene*]-3-*o*-*tolyl*-2 *o*-*tolylimino*-4 *thiazolidone*.—A mixture of 3-*o*-tolyl-2-*o*-tolylimino-4-thiazolidone (0.3 g.) and 2-(4-acetanilido-1 : 3-butadienyl)-benzimidazole methiodide (0.45 g.) was refluxed in acetic anhydride in presence of fused sodium acetate and isolated as the previous compound, m.p. >300°, yield 53%. (Found : C, 72.85 ; H, 5.44. $C_{30}H_{28}ON_4S$ requires C, 73.17 ; H, 5.69%).

5-[4-(1 : 3-*Dimethylbezimidazolin-2-ylidene*)-*buten-1-ylidene*]-3-p-*tolyl*-2-p-*tolylimino*-4-*thiazolidone* was prepared and isolated exactly in the manner described above by refluxing 0.3 g. of 3-*p*-tolyl-2-*p*-tolylimino-4-thiazolidone and 0.45 g. of 2-(4-acetanilido-1 : 3-butadienyl)-benzimidazole methiodide, m.p. >300°, yield 50%. (Found : C, 73.02; H, 5.48. $C_{30}H_{28}ON_4S$ requires C, 73.17 ; H, 5.69%).

5-[6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-1-ylidene*]-2-*phenylimino*-4-*thiazolidone* was prepared similarly by refluxing nearly 0.2 g. of 2-phenylimino-4-thiazolidone with 0.47 g. of 2-(6-acetanilido-1 : 3 : 5-hexatrienyl)-benzimidazole methiodide. It was filtered, washed with acetone and finally recrystallised from hot methanol, m.p. >300°, yield 68%. (Found : C, 69.13 ; H, 5.08. $C_{24}H_{22}ON_4S$ requires C, 69.56 ; H, 5.31%).

5-[6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-1-ylidene*]-2-α-*naphthylimino*-4-*thiazolidone* was obtained as usual from 2-α-naphthylimino-4-thiazolidone (0.24 g.) and 2-(6-acetanilido-1 : 3 : 5-hexatrienyl)-benzimidazole methiodide (0.47 g.) at 150°. It was cooled, washed thoroughly with water and finally recrystallised from methanol, m.p. >300°, yield 58%. (Found : C, 72.08 ; H, 4.83. $C_{28}H_{24}ON_4S$ requires C, 72.41 ; H, 5.17%).

5-[6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-2-ylidene*]-β-*naphthylimino*-4-*thiazolidone* was prepared similarly as above by refluxing 2-β-naphthylimino-4-thiazolidone (0.24 g.) and 2-(6-acetanilido-1 : 3 : 5-hexatrienyl)-benzimidazole methiodide (0.47 g.) in acetic anhydride and was also isolated similarly, m.p. >300°, yield 50%. (Found : C, 72.12 ; H, 5.02. $C_{28}H_{24}ON_4S$ requires C, 72.41 ; H, 5.17%).

5-[6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-1-ylidene*]-3-*phenyl*-2-*phenylimino*-4-*thiazolidone* was prepared as above by refluxing 3-phenyl-2-phenylimino-4-thiazolidone (0.27 g.) and 2-(6-acetanilido-1 : 3 : 5-hexatrienyl)-benzimidazole methiodide (0.47 g.). It was cooled, stirred with water and kept overnight. The product was cooled, washed well with cold water followed by acetone and finally recrystallised from methanol, m.p. 210° (decomp.), yield 48%. (Found : C, 73.18; H, 5.13. $C_{30}H_{26}ON_4S$ requires C, 73.40 ; H, 5.30%).

5-[6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-1-ylidene*]-3-o-*tolyl*-2-o-*tolylimino*-4-*thiazolidone*.—3-*o*-Tolyl-2-*o*-tolylimino-4-thiazolidone (~0.15 g.) and 2-(6-acetanilido-1 : 3 : 5-hexatrienyl)-benzimidazole methiodide (0.24 g.) in 6 c.c. of acetic anhydride were heated under reflux for 3 hours in presence of fused sodium acetate. It was cooled, washed repeatedly with water and recrystallised from methanol, m.p. >300°, yield 50%. (Found : C, 73.81 ; H, 5.43. $C_{32}H_{30}ON_4S$ requires C, 74.13 ; H, 5.79%).

5 [6-(1 : 3-*Dimethylbenzimidazolin-2-ylidene*)-*hexa-2 : 4-dien-7-ylidene*]-3-p-*tolyl*-2-p-*tolylimino*-4-*thiazolidone* was prepared similarly as its *o*-tolyl analogue from 0.15 g. of 3-*p*-tolyl-2-*p*-tolylimino-4-thiazolidone, and isolated similarly, m.p. 203° (decomp.), yield 45%. (Found : C, 74.01 ; H, 5.73. $C_{32}H_{30}ON_4S$ requires C, 74.13 ; H, 5.79%).

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FRIES TRANSFORMATION OF CONDENSATES OF SEBACIC ACID WITH PHENOLS: 1:8-DIBENZOYL-OCTANES

By J. P. Varma and J. S. Aggarwal

Diaryl esters have been obtained, in high yields, by condensing sebacic acid with several monohydric phenols in presence of sulphonic acid catalysts. In the case of α- and β-naphthols and resorcinol, the Fries transformation to the corresponding diketones takes place partly; with other dihydric phenols, the esterification results in the formation of resinous products. The diaryl esters, converted by the Fries transformation to the corresponding diketones, have further been reduced by the Clemmensen reduction.

Excepting the use of succinic and adipic acids, long chain dicarboxylic acids do not appear to have been employed for the preparation of diaryl diketones (Etaix, *Ann. chim. phys.*, 1896, *vii*, **9**, 372). In order to study the course of reaction and the types of products obtained, the condensation products of sebacic acid with various mono- and dihydric phenols have been converted, through the Fries transformation, into 1:8-dibenzoyl-octanes. These phenolic diaryl diketones have been further reduced by the Clemmensen reduction to the corresponding diaryl decanes, which are likely to be effective antioxidants, these being similar to nor-dihydroguaiaretic acid (NDGA) in constitution. The long hydrocarbon chain is likely further to afford an increased solubility to these compounds in various oils and fats.

Condensation of Phenols with Sebacic Acid.—The esterification of phenols with fatty acids had been rather difficult till recently, as it involved the prior preparation of acid chlorides (Conant and Blatt, "The Chemistry of Organic Compounds", Macmillan & Co., New York, 1947, p. 430; Adams *et al.*, "Organic Reactions", Wiley, New York, 1947, p. 353) and anhydrides. Bader and Kontowicz (*J. Amer. Chem. Soc.*, 1953, **75**, 5416) have reported the preparation of phenyl esters in 60-65% yield by heating directly the free acids with phenol in presence of polyphosphoric acid. In this process, however, 4 to 4.5 moles of phenol per mole of acid and substantial quantities of condensing agents were found desirable.

Aelony (*J. Amer. Oil Chem. Soc.*, 1955, **32**, 170) by using 1-2% concentrated sulphuric acid and removing the water of esterification azeotropically, could directly esterify mono- and dihydric phenols with various monocarboxylic acids in satisfactory yields. The reaction products, however, were dark and their purification was difficult. Other catalysts, such as phosphoric acid, zinc stearate, lead stearate, triphenyl phosphate, were found not so efficient. In the present investigation, it has been found that the use of *p*-toluenesulphonic acid or naphthalene-2-sulphonic acid as catalyst for the condensation of sebacic acid with phenols furnishes very clear products in good yields (70-90%).

In the case of α- and β-naphthols and resorcinol, it was observed that during the course of esterification, the Fries reorientation also took place partly, affording mixtures of ketones and esters. This may be due to the greater reactivity of

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the naphthol molecule. As usual, the condensation in the case of β-naphthol probably takes place at position-1 in preference to 3. An identical product was also isolated by the Friedel-Crafts reaction. Acylation of α-naphthol, however, by the Friedel-Crafts method gave both *o*- and *p*-hydroxyketones while by using sulphonic acid as catalyst, only *o*-isomer could be isolated. The *o*-isomer was identified by the fact that on treatment with alcoholic ferric chloride solution an intense coloration was obtained, whereas the *p*-isomer showed no colour.

The same diketone, 1:8-di(2:4-dihydroxy-1-benzoyl)-octane (**X**), in low yield (10%) along with a very small amount of a fluorescent dye was also obtained when equimolecular proportions of sebacic acid and resorcinol were condensed in presence of two moles of zinc chloride as also was obtained by von Braun *et al.* (*Ber.*, 1941, **74B**, 1772).

Esterification of hydroquinone and catechol with equimolecular proportion of sebacic acid gave only resinous products which most probably were due to the pol. ester formation.

Fries Rearrangement of the Diaryl Esters.—The Fries rearrangement of the diaryl esters was successfully carried out by 2.2 moles of anhydrous aluminium chloride at a temperature not exceeding 60°. At higher temperatures resinification of the products took place. Under these conditions it was observed that *p*-dicresyl sebacate gave only *o*-hydroxyketone and *o*-dicresyl sebacate favoured the formation of the *p*-hydroxy product. These ketones were obtained in 50-60% yield. In the case of phenol, the yield of *o*-isomer was 21% and that of *p*-isomer, 40%. The *o*- and *p*-hydroxyketones were separated by the preferential solubility of the *p*-isomer in 1% NaOH solution.

The Clemmensen reduction of diaryl diketones was carried out by the Martins modification (*J. Amer. Chem. Soc.*, 1936, **58**, 1438) as described in the experimental portion.

EXPERIMENTAL

Esterification of Phenol with Sebacic Acid.—A mixture of phenol (0.1 *M*), sebacic acid (0.05 *M*), xylene (60 c.c.) and *p*-toluenesulphonic acid (1 g.) was taken in a 250 c.c. r.b. flask fitted with a water trap of Dean-Stark type. The flask was heated in an oil-bath at 170-80°, when about 80% of the theoretical quantity of water collected during first 6 hours of heating. Almost the theoretical quantity of water was obtained after the next 6 hours. The reaction product was diluted with more xylene (*ca.* 200 c.c.) and washed first with a 2% NaOH solution and then with water till free of alkali, dried (sodium sulphate) and the solvent distilled off under reduced pressure. The residue (*ca.* 90%) was twice crystallised from light petroleum. The various characteristics of the product, thus obtained, and those derived from other phenols are recorded in Table I.

Friedel-Crafts Reaction with α- and β-Naphthols.—Sebacyl chloride was prepared by the action of thionyl chloride on sebacic acid and purified by vacuum distillation.

TABLE I

Condensation of sebacic acid and sebacyl chloride with phenols.

Phenols.	Catalyst employed.	Products obtained. Name.	Formula.	Cryst. from.	M.P.	Yield.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc	Remarks.
Phenol	*A	Diphenyl sebacate (I)	$C_{22}H_{26}O_4$	Light petroleum	62°	90%	74.6	74.55	7.8	7.89	Colorless crystalline product.
p-Cresol	*B	*p*-Dicresyl sebacate (II)	$C_{24}H_{30}O_4$	,,	76.5°	88	74.9	75.36	7.8	7.91	,,
m-Cresol	A	*m*-Dicresyl sebacate (III)	$C_{24}H_{30}O_4$	,,	55°	70	75.2	75.36	7.9	7.91	,,
o-Cresol	B	*o*-Dicresyl sebacate (IV)	$C_{24}H_{30}O_4$	...	(b.p.) 157°/ 2-2.5 mm.	85	74.8	75.36	7.9	7.91	Pale yellow liquid.
α-Naphthol	A	1:8-Di(1-hydroxy-2-naphthoyl)-octane (V).	$C_{30}H_{30}O_4$	Benzene	123°	40	79.7	79.27	6.6	6.65	Keto band at 276 mμ in U.V.; positive $FeCl_3$ test.
,,	*C	Do (VI)	$C_{30}H_{30}O_4$	,,	122°	13	78.9	79.27	7.1	6.65	Positive $FeCl_3$ test; mixed m.p. with (V) 122-23°.
,,	C	1:8-Di(1-hydroxy-4-naphthoyl)-octane (VII)	$C_{30}H_{30}O_4$	,,	140°	8	79.0	79.27	6.9	6.65	$FeCl_3$ test negative.
β-Naphthol	A	1:8-Di(2-hydroxy-1-naphthoyl)-octane (VIII)	$C_{30}H_{30}O_4$	,,	88°	60	79.1	79.27	6.2	6.65	Keto band at 276 mμ in U.V.; positive $FeCl_3$ test.
,,	C	Do (IX)	$C_{30}H_{30}O_4$	,,	87°	24	79.27	79.27	6.75	6.65	Positive $FeCl_3$ test; mixed m.p. with (VIII) 88°.
Resorcinol	A	1:8-Di(2:4-dihydroxybenzoyl)-octane (X)	$C_{22}H_{26}O_6$	,,	168°	30	68.2	68.38	7.3	6.78	Mixed m.p. with the product obtained with $ZnCl_2$ 168°.
Hydroquinone	A	Resinous product obtained.									
Catechol	A	Resinous product obtained.									

*A = *p*-toluenesulphonic acid. *B = Naphthalene-2-sulphonic acid. *C = Friedel-Crafts catalyst ($AlCl_3$) with sebacyl chloride.

TABLE II

Fries rearrangement of phenol esters.

*Phenol ester taken.	Product on rearrangement.	Formula.	M.P.	Yield.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.	Remarks.
	1 :8-Di(*o*-hydroxybenzoyl)-octane (XI)	$C_{22}H_{26}O_4$	101-102°	21%	74.8	74.55	7.1	7.39	Gave a keto band at 276 mμ in U.V. In ethanol gave intense coloration with $FeCl_3$. Its oxime crystallised from MeOH, m.p. 145°. (Found: N, 6.8. $C_{22}H_{28}O_4N_2$ requires N, 7.3%).
(I)	1 :8-Di(*p*-hydroxy benzoyl)-octane (XII)	$C_{22}H_{26}O_4$	136°	40	74.8	74.55	7.3	7.39	Crystallised from benzene.
	1 :8-Di(2-hydroxy-3-methyl-benzoyl)-octane (XIII)	$C_{24}H_{30}O_4$	106°	13	75.7	75.36	8.4	7.91	Gave a keto band at 275 mμ in U.V. and intense coloration with $FeCl_3$. Oxime crystallised from EtOH, m.p. 170°. (Found: N, 6.8. $C_{24}H_{32}O_4N_2$ requires N, 6.8%).
(IV)	1 :8-Di(3-methyl-4-hydroxy-benzoyl)-octane (XIV)	$C_{24}H_{30}O_4$	196°	47	75.4	75 36	8.5	7.91	Crystallised from benzene.
(III)	1 :8-Di(2-hydroxy-4-methyl-4-hydroxybenzoyl)-octane (XV)	$C_{24}H_{30}O_4$	120.5°	53	75.3	75.36	8.3	7.91	Gave a keto band at 276 mμ in U.V. Intense colour with $FeCl_3$. Crystallised from MeOH.
(II)	1 :8-Di(2-hydroxy-5-methyl-benzoyl)-octane (XVI)	$C_{24}H_{30}O_4$	110.5°	62	75.1	75.36	8.0	7.91	Gave a keto band at 276 mμ in U.V. Deep colour with $FeCl_3$. Crystallised from benzene. Oxime crystallised from EtOH, m.p. 178°. (Found: N, 6.7. $C_{24}H_{32}O_4N_2$ requires N, 6 8%).

* Vide Table I, column 3.

TABLE III

Clemmensen reduction of diaryl diketones.

* Diaryl diketone taken.	Reduced products.	Formula.	Cryst. from.	M.P.	Yield.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
(XII)	1 :10-Di(*p*-hydroxyphenyl)-decane (XVII)	$C_{22}H_{30}O_2$	Benzene	132°	86%	81 2	80.93	9.1	9.26
(XIV)	1 :10-Di(3-methyl-4-hydroxy-phenyl)-decane (XVIII)	$C_{24}H_{34}O_2$	Xylene	98°	90	81.3	81.31	9.7	9.67
(XVI)	1 :10 Di(2-hydroxy-5-methyl-phenyl)-decane (XIX)	$C_{24}H_{34}O_2$	Benzene	88°	87	81.2	81.31	9.7	9.67
(XV)	1 :10-Di(2-hydroxy-4-methyl-phenyl)-decane (XX)	$C_{24}H_{34}O_2$	,,	79°	88	81.3	81.31	9.3	9.67

* Vide Table II, column 2.

α- or β-naphthol (0.1 *M*) in tetrachlorethane (70 c.c.) was taken in a 250 c.c. 3-necked flask fitted with a mercury-sealed stirrer, condenser and dropping funnel. The contents of the flask were cooled to 10° and powdered anhydrous aluminium chloride (0.11 *M*) was added at such a rate that the temperature did not rise above 15°. The cooling bath was removed and sebacyl chloride (0.05 *M*) was introduced through a dropping funnel over a period of 30 minutes. The contents of the flask were heated and constantly stirred at 50-60° for 4 hours. The mixture, after cooling, was decomposed by pouring over crushed ice containing dilute HCl. The solvent and any free phenol were removed from the reaction product by steam-distillation. The separation of *o*- and *p*-hydroxyketones was effected by the preferential solubility of the *p*-isomer in 1% NaOH solution. The characteristics of the products, thus obtained, are also shown in Table I.

Fries Rearrangement of Diphenyl Sebacate.—A mixture of diphenyl sebacate (0.05 *M*) and tetrachlorethane (55 c.c.) was taken in a 3-necked flask equipped with a mercury-sealed stirrer and a thermometer. Powdered anhydrous aluminium chloride (0.11 *M*) was added in small lots and the mixture heated for 4 hours at 50-60°. The reaction product was poured over crushed ice containing dilute HCl and then steam-distilled to remove the solvent. The residue was cooled and extracted with ether. The ethereal solution was shaken with 1-2% solution several times till the aqueous layer was almost colorless. The ether solution was washed with water and dried (Na_2SO_4). After removal of the solvent, the residue was crystallised from benzene. The alkaline extract was acidified with HCl and heated to boiling to remove the ether. The residue was cooled and the solid was separated and crystallised from benzene. The characteristics of these products and also those obtained from other phenol esters are recorded in Table II.

Clemmensen Reduction of Diketones.—Zinc wool (22 g.) was taken in a 3-necked flask fitted with mercury-sealed stirrer, condenser and a tube joined to Kipp's apparatus for passing HCl gas. Mercuric chloride (2.5 g.), dissolved in 25 c.c. of water and 2 c.c. of HCl (conc.), was added to the zinc wool and shaken for 10 minutes till the amalgamation was complete. Water layer was decanted off and HCl (1 : 1) was added just to cover one half of the amalgamated zinc. The diketone (5 g.), dissolved in xylene (30 c.c.), was then added. The flask was heated in an oil-bath with continuous stirring. The temperature in the initial stage was maintained at 90-100° and was gradually raised to 150° as the reaction proceeded. Xylene layer was separated at the end of the reaction, washed free of mineral acid, dried (Na_2SO_4), solvent distilled off and the residue was crystallised from benzene or xylene. The characteristics of various products are recorded in Table III. U.V. spectrum of all the products showed the absence of the keto band.

All the compounds recorded in Tables I to III are new, except 1:8-di(2 : 4-dihydroxy-1-benzoyl)-octane (X).

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* Vide Table II, column 2.

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THE STRUCTURE OF TETUIN

By C. R. Mehta and T. P. Mehta

Tetuin, a glycoside, has been isolated from the seeds of *Oroxylum indicum* Vent. and has been shown from the study of its properties, reactions, etc. and those of its derivatives, to be baicalein-6-glucoside.

Oroxylum indicum Vent. (N. O. Bignoniaceae) grows throughout India. The root bark is of considerable importance in Aurvedic medicine and is an ingredient of the well-known decoction of ten roots called Dashmulasava (Kirtikar and Basu, "Indian Medicinal Plants", Vol. III, Lalit Mohan Basu, Allahabad, 1933, p.1839). Besides baicalein, phytosterol and galactose, a yellow crystalline colouring matter, Oroxylin-A (5: 7-dihydroxy-6-methoxyflavone ; Shah, Mehta and Wheeler, *J. Chem. Soc.*, 1936, 591 ; 1938, 1555), the structure of which has been confirmed by the synthesis of its diethyl ether (Row, Shastry, Seshadri and Thiruvengadam, *Proc. Ind. Acad. Sci.*, 1949, **28A**, 189), has been isolated from the root bark. Seeds are used in Gujarat as a household remedy for hysteria and broncho-pneumonia and have been found to be purgative. It was therefore considered desirable to investigate the seeds. In course of the examination of the seeds, a non-drying fixed oil, a yellow crystalline substance, m.p. 274° (Mehta, *Proc. Ind. Acad. Sci.*, 1939, **9A**, 390), baicalein (Mehta and Mehta, *Curr. Sci.*, 1943, **12**, 274) and a pale yellow crystalline substance, named *Tetuin* (*ibid.*, 1953, **22**, 114), have been obtained.

The present paper describes the results of our investigations on Tetuin. Spontaneous evaporation of the alcohol extract after removal of baicalein left a sticky solid which on treatment with pyridine and repeated crystallisations from methyl alcohol yielded a pale yellow crystalline substance, m.p. 112-14°, sintering at 77-78° (yield 0.6%), responding to tests for glycosides. Seeds used in the present investigation were collected from the Songhad forests in Gujarat.

Our conclusions on the structure of Tetuin are based on the following observations :

(*a*) Its molecular formula arrived at from analytical results is $C_{21}H_{20}O_{10}$, $2H_2O$.
(*b*) It gives magnesium-hydrochloric acid-xanthoxine reaction.
(*c*) It does not contain methoxyl group.
(*d*) It forms a hexa-acetyl derivative.
(*e*) It does not reduce Fehling's solution but does so only after acid hydrolysis.
(*f*) Dilute mineral acid splits it into a substance of m.p. 265-66° and glucose.

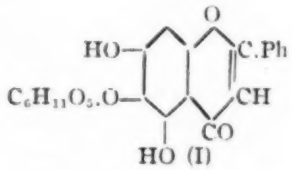
$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6.$$

The former and its derivatives agree in reactions, properties, etc., with those of baicalein (5 : 6 : 7-trihydroxyflavone) and its derivatives (Shibata *et al.*, *Acta Phytochim.*, 1923, **1**, 105 ; Bargellini, *Gazzetia*, 1919, **49**, 47). Its melting

point is undepressed on admixture with authentic baicalein, very kindly supplied by Prof. Shibata, to whom we express our thanks. Glucose has been identified as its osazone. These results show that tetuin is a flavone glucoside.

(*g*) It gives a reddish violet coloration with alcoholic ferric chloride unlike primetin (Nagai and Hattori, *Acta Phytochim.*, 1930, **5**, 1) which gives a green colour.

(*h*) It does not give a brown coloration with ammonium molybdate and acetic acid (Quastel, *Analyst*, 1931, **56**, 311) nor does it reduce ammoniacal silver nitrate. Oroxylin-A does not answer this test (Shah, Mehta and Wheeler, *loc. cit.*). Tetuin is therefore, in all probability, baicalein-6-glucoside (I). The synthesis of (I) is in progress.



(I)

EXPERIMENTAL

Extraction of Tetuin.—Seeds (500 g.) of *Oroxylum indicum* Vent. were powdered, defatted with petroleum ether (b.p. 35-60°) and extracted with alcohol in a Soxhlet apparatus. After removal of a greater portion of alcohol by distillation under reduced pressure and on spontaneous evaporation, a yellow-coloured extract was obtained. This was extracted with ether and chloroform, refluxed with alcohol (charcoal) for an hour and filtered. On keeping the solution in a refrigerator overnight a deep yellow subtance separated. This was filtered and crystallised successively from aqueous alcohol, glacial acetic acid and xylene when deep yellow needles (m.p. 265-66°) were obtained. The substance has been identified from its properties, reactions and mixed melting point as baicalein (5 : 6 : 7-trihydroxyflavone) which is also obtained as one of the products on acid hydrolysis of the glycoside. The alcoholic mother-liquor, after complete removal of baicalein, left a sticky residue after several days. The residue was treated with pyridine and refluxed with methanol (charcoal). Repeated crystallisations from the latter solvent furnished pale yellow crystals of tetuin, m.p. 112-14°, sintering at 77-78°, yield 0.6%.

Tetuin is soluble in water, ethyl alcohol, methyl alcohol, pyridine, dilute alkali and insoluble in petroleum ether, ether, benzene, etc. It does not reduce Fehling's solution but does so only on acid hydrolysis. With magnesium and hydrochloric acid in aqueous alcoholic solution it develops an organge-red colour. Its alcoholic solution exhibits a blackish green colour with alcoholic ferric chloride. (Found : C, 53.6 ; H, 4.9. $C_{21}H_{24}O_{12}$ requires C, 53.8 ; H, 5.1%).

Hexa-acetyltetuin (acetic anhydride-anhydrous sodium acetate) separated from alcohol in colorless needles, m.p. 268-69°. It is insoluble in alkali and does not give any coloration with alcoholic ferric chloride. (Found : C, 57.7 ; H, 4.6. $C_{33}H_{32}O_{16}$ requires C, 57.9 ; H, 4.7 %).

Hydrolysis of Tetuin with dilute Acid: Isolation of Baicalein.—The substance (2.0 g.) was boiled under reflux with 100 c.c. of 5% HCl for 2 hours; a yellow crystalline solid separated within 15 minutes. The precipitate (A) and the filtrate (B) were separately examined as follows.

The precipitate (A) was washed with water, crystallised from aqueous alcohol, glacial acetic acid and xylene, when bright yellow needles of a substance, m.p. 265-66°, were obtained. It shows the following reactions:

(*i*) A trace of sodium amalgam produces green flocks when added to its alcoholic solution.

(*ii*) It dissolves in dilute alkali with reddish brown coloration followed by green flocks.

(*iii*) Alcoholic ferric chloride, when added to its alcoholic solution, gives a brownish black colour.

(*iv*) The melting point of the substance was not depressed on admixture with authentic baicalein to which it corresponded in its properties. (Found: C, 66.2; H, 3.5. Calc. for $C_{15}H_{10}O_5$: C, 66.6; H, 3.7%).

(*v*) Acetylation of the substance (acetic anhydride-anhydrous sodium acetate) gave a derivativ , m. p. 190-91°, the m. p. recorded for triacetyl-baicalein (5:6:7-triacetoxyflavone) being 191-92° (Bergellini, *loc. cit.*). (Found: C, 63.5; H, 3 8. Calc. for $C_{21}H_{16}O_8$: C, 63.6; H, 4.0%).

(*vi*) Methylation of the substance with diazomethane, followed by treatment with methyl sulphate and 20% KOH in boiling acetone solution, yielded a derivative, m.p. 164-65°, that recorded for trimethyl-baicalein (5:6:7-trimethoxyflavone) being 165-66° (Bargellini, *loc. cit.*). It does not dissolve in alkali and shows no coloration with alcoholic ferric chloride. (Found: C, 68.8; H, 5.6. Calc. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.7%).

The filtrate (B) was neutralised with barium carbonate, concentrated to a small bulk and treated with phenylhydrazine in acetic acid solution. The osazone, after three crystallisations from alcohol (charcoal), melted at 204°, unchanged when mixed with a pure sample of glucosazone.

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KOSTANECKI-ROBINSON PHENYLACETYLATION OF ORCACETOPHENONE AND ORCPROPIOPHENONE

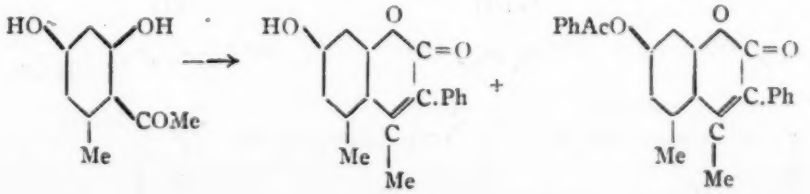
By C. B. Thanawalla and P. L. Trivedi

Phenylacetylation of orcacetophenone and orcpropiophenone has been carried out by the Kostanecki-Robinson method, affording 7-phenylacetoxy-3-phenyl-4 :5-dimethylcoumarin (II, m.p. 179-80°) and a mixture of 7 phenylacetoxy-2- (X, m.p. 111-12°) and 7-hydroxy-2-benzyl-3 :5-dimethylchromone (XI, m.p. 245-47°) respectively.

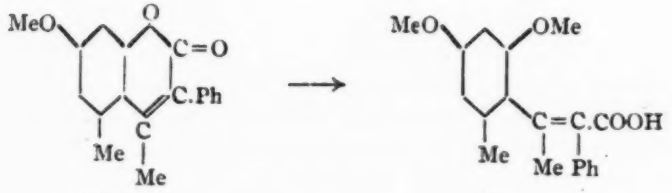
It was observed by Heilbron *et al.* (*J. Chem. Soc.*, 1936, 295) that when resacetophenone was subjected to the Kostanecki-Robinson phenylacetylation, it afforded exclusively a coumarin, while respropiophenone under similar conditions furnished mainly a coumarin, with only traces of chromone. It was therefore thought of interest to study the behaviour of orcacetophenone and orcpropiophenone on the Kostanecki-Robinson phenylacetylation.

The phenylacetylation of orcacetophenone was carried out by heating a mixture of orcacetophenone (I), fused sodium phenylacetate and phenylacetic anhydride under the usual conditions of the Kostanecki-Robinson reaction. The reaction afforded 7-phenylacetoxy-3-phenyl-4 : 5-dimethylcoumarin (II : m.p. 179-80°). This afforded 7-hydroxy-3-phenyl-4: 5-dimethylcoumarin (III : m. p. 245-47°) on hydrolysis with 80% sulphuric acid. The structure assigned to these compounds is based on the degradation of the methyl ether of 7-hydroxy-3-phenyl-4:5-dimethylcoumarin (IV) to the corresponding cinnamic acid derivative (V), and such an assignment has further been supported by the synthesis of isomeric 7-methoxy-2-benzyl-5-methylchromone (VI), which has been found to be different from (IV).

The hydrolysis of (IV) to the corresponding cinnamic acid derivative (V) was carried out by caustic alkali in presence of dimethyl sulphate. The synthesis of (VI) was carried out by the Claisen condensation of orcacetophenone dimethyl ether (VII) with ethyl phenylacetate in presence of sodium, which afforded a β-diketone, 2 :4-dimethoxy-6-methylbenzoylphenylacetyl-methane (VIII). This was then cyclised to (VI) by means of hydrobromic acid in acetic acid.



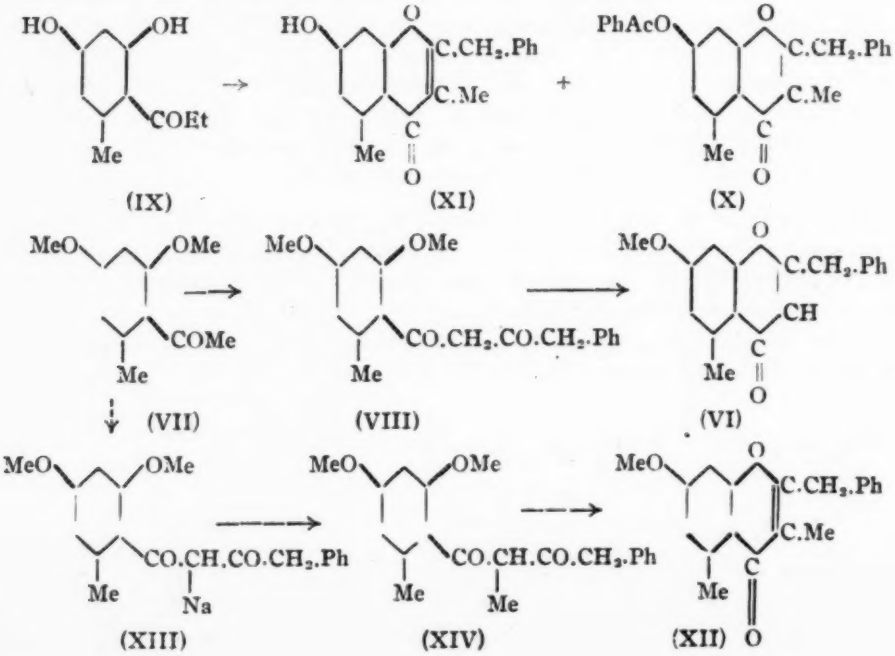
(I) (II) (III)



(IV) (V)

The Kostanecki-Robinson phenylacetylation of orcpropiophenone (IX) was carried out in much the same way as in the case of orcacetophenone. This furnished a mixture of 7-phenylacetoxy-2-benzyl-3 : 5-dimethylchromone (X : m.p. 111-12°) and 7-hydroxy-2-benzyl-3 : 5-dimethylchromone (XI : m.p. 248-49°). The former could also be converted into the latter by means of 80% sulphuric acid. The structure assigned to these products is based on the synthesis, through an unambiguous method, of 7-methoxy-2-benzyl-3 : 5-dimethylchromone (XII), which has been found to be the same as the methoxy derivative of (XI). The structure of a chromone is further supported by its stability towards dilute alkali.

The synthesis of (XII) consisted in the Claisen condensation of the orcacetophenone dimethyl ether (VII) with ethyl phenylacetate in presence of sodium, methylation of the sodium salt (XIII) furnishing the β-diketone, 2 : 4-dimethoxy-6-methylbenzylphenylacetyl-ethane (XIV), which unfortunately could not be isolated in the pure form, and cyclisation of the β-diketone (XIV) to (XII) by means of hydrobromic acid in acetic acid.



(VII) (VIII) (VI)

(XIII) (XIV) (XII)

EXPERIMENTAL

Phenylacetylation of Orcacetophenone: 7-Phenylacetoxy-3-phenyl-4·5-dimethylcoumarin.—Orcacetophenone (2 g.), fused sodium phenylacetate (6 g.) and phenylacetic anhydride (20 g.) were heated in an oil-bath at 180-90° for about 8 hours. The brown mass obtained was treated with CS_2 (100 c.c.) to remove excess of phenylacetic anhydride. It was then treated with water to remove sodium phenylacetate. It was finally treated with a dilute solution of sodium bicarbonate and then with water. The crude product, thus obtained, was crystallised from alcohol in slender needles, m.p. 179-80°, yield 1.2 g. This was found to be 7-phenylacetoxy-3-phenyl-4:5 dimethylcoumarin. It is insoluble in alkali and does not exhibit any coloration with ferric chloride. (Found: C, 77.8; H, 5.2. $C_{25}H_{20}O_4$ requires C, 78.1; H, 5.3%).

7-Hydroxy-3-phenyl-4:5-dimethylcoumarin.—The above coumarin (1 g.) was kept overnight in contact with H_2SO_4 (80%, 5 c.c.). The solution was then poured in cold water when a slightly orange-coloured precipitate separated. It was crystallised from rectified spirit in tiny needles, m.p. 246-47°, yield 0.05 g. (Found: C, 77.1; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%).

7-Methoxy-3-phenyl-4:5-dimethylcoumarin was prepared by refluxing the above 7-hydroxycoumarin derivative (0.6 g.), dissolved in dry acetone (100 c.c), with methyl iodide (6 c.c.) in presence of fused potassium carbonate (1 g.) for 15 hours. After removal of most of the acetone, the reaction mixture was diluted with water. The product obtained was crystallised from alcohol in long needles, m.p. 148-49°, yield 0.2 g. Mixed m.p. with the corresponding chromone, as described below, was depressed by 20°. (Found: C, 77.4; H, 5.5. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%).

Hydrolysis of 7-Methoxy-3-phenyl-4:5-dimethylcoumarin: 2:4 Dimethoxy-6-methyl-α-phenyl-β-methylcinnamic Acid.—7-Methoxy-3-phenyl-4:5-dimethylcoumarin (1 g.) was dissolved in acetone (20 c.c.). To the warm solution were added dimethyl sulphate (3 c.c.) and sodium hydroxide (10%, 30 c.c.) with constant shaking. The reaction mixture was then heated to boiling under reflux. More dimethyl sulphate (12 c.c. in all) and sodium hydroxide (10%, 100 c.c. in all) were added alternately, stirring being continued during the above additions. Finally, excess of sodium hydroxide (10%, 18 c.c.) was added to make the reaction mixture distinctly alkaline. It was refluxed for half an hour and allowed to stand overnight at room temperature. Next day it was filtered and the filtrate was acidified with HCl (conc.), when a light yellow substance separated. This was filtered and treated with dilute sodium bicarbonate solution and filtered. The filtrate on acidification with HCl afforded a white substance which was crystallised from alcohol in colorless needles, m.p. 179-80°, yield 0.06 g. This was found to be 2:4-dimethoxy-6-methyl-α-phenyl-β-methylcinnamic acid. It did not give any coloration with alcoholic ferric chloride. (Found: C, 72.6; H, 6.3. $C_{19}H_{20}O_4$ requires C, 72.9; H, 6.3%).

Claisen Condensation of Orcacetophenone Dimethyl Ether with Ethyl Phenylacetate: 2-:4-*Dimethoxy-6-methylbenzoylphenylacetyl-methane*.—A solution of orcacetophenone dimethyl ether (6 g., 1*M*) and ethyl phenylacetate (17 g., 4*M*) in dry xylene, was gradually added to the flask containing pulverised sodium (1.5 g., 2 moles suspended in dry xylene), the container being kept cool by cold water. After the initial reaction had subsided, the reaction mixture was heated at 130° in an oil-bath for 2 hours. After the decomposition of excess of sodium by addition of water, the reaction mixture was then extracted with ether to remove unchanged ethyl phenylacetate and orcacetophenone dimethyl ether and xylene. The aqueous solution was then acidified with dilute acetic acid when an oil separated. After drying in a vacuum desiccator, it was distilled under reduced pressure and the fraction distilling at 225-30°/0.5 mm was collected. It solidified on keeping for four days. It was crystallised from methanol, m.p. 69-70°, yield 1 g. It was found to be 2 : 4-dimethoxy-6-methylbenzoylphenylacetyl-methane. (Found : C, 72.9 ; H, 6.2. $C_{19}H_{20}O_4$ requires C, 72.9 ; H, 6.4%).

The *copper salt* was prepared by shaking the above product, dissolved in ether, with a saturated solution of copper acetate for half an hour, when a green powdery mass separated. It was filtered and crystallised from petroleum ether-benzene mixture (5 : 1) in tiny prisms, m.p. 145-46°. (Found : C, 66.2 ; H, 5.3 ; Cu, 9.5. $C_{38}H_{38}O_8Cu$ requires C, 66.5 ; H, 5.5 ; Cu, 9.2%).

7-Methoxy-2-benzyl-5-methylchromone.—The above β-diketone (0.5 g.) was treated with hydrobromic acid in acetic acid (35%, 2 c.c.), and the mixture was allowed to stand overnight. Next day, it was poured in ice-water when a pasty mass separated. This was treated with alkali and filtered. The residue was crystallised from methyl alcohol in fine needles, m.p. 142-44°, yield 0.2 g. (Found : C, 77.3 ; H, 5.4. $C_{18}H_{16}O_3$ requires C, 77.1 ; H, 5.7%).

Phenylacetylation of Orcpropiophenone : *7-Hydroxy-2-benzyl-3:5-dimethylchromone* (A).—Orcpropiophenone (2 g.), fused sodium phenylacetate (6 g.) and phenylacetic anhydride (20 g.) were heated at 160-70° in an oil-bath for 8 hours. The reaction mixture, which solidified to a pasty mass on cooling, was refluxed with petroleum ether (b.p. 40-60°, 150 c.c.) and was filtered hot. The residue after washing with water was crystallised from hot acetic acid in white tiny crystals, m.p. 248-49°, yield 0.2 g. It was found to be 7-hydroxy-2-benzyl-3 : 5-dimethylchromone. It is soluble in alkali. (Found : C, 76.9 ; H, 5.9. $C_{18}H_{16}O_3$ requires C, 77.1 ; H, 5.7%).

7-Phenylacetoxy-2-benzyl-3 : 5-dimethylchromone (B).—The petroleum ether filtrate from the above, on complete removal of the solvent, gave a pasty mass. This was extracted with ether and the ether extract was washed with dilute sodium bicarbonate solution in order to remove phenylacetic acid formed during the reaction. The ether extract was further washed with water and dried over anhydrous sodium sulphate. On removal of ether, a thick yellow oil was obtained. This was triturated with absolute alcohol, when a white solid separated. It was filtered and crystallised from alcohol in tiny needles, m.p. 111-12°, yield 0.9 g. It was found to be 7-phenylacetoxy-2-benzyl-3 : 5-dimethylchromone. It is insoluble in alkali. (Found : C, 78.5 ; H, 5.6. $C_{26}H_{22}O_4$ requires C, 78.4 ; H, 5.5%).

On working up the alcoholic filtrate, obtained from the trituration of the above oil by sulphuric acid (80%, 5 c.c.) treatment, a further quantity of 7-hydroxy-2-benzyl-3 : 5-dimethylchromone (0.2 g.) was obtained.

7-Hydroxy-2-benzyl-3:5-dimethylchromone.—The condensation product (B, 1 g.) was left overnight with H_2SO_4 (80%, 10 c.c.). Next day, the reaction mixture was poured in ice-water. The product separating was crystallised from acetic acid in tiny needles, m.p. 248-49°, yield 0.4 g. Mixed m.p. with (A) did not depress.

7-Methoxy-2-benzyl-3:5-dimethylchromone.—The product (A, 0.25 g.), dissolved in dry acetone (60 c.c.), was refluxed for ten hours with methyl iodide (3 c.c.) in presence of fused potassium carbonate (1 g.). After the removal of most of the acetone, the reaction mixture was diluted with water. The product obtained was crystallised from alcohol in small stout needles, m.p. 125-26°, yield 0.1 g. It is insoluble in alkali. Mixed m.p. with the authentic specimen described below did not depress. (Found: C, 77.3 ; H, 5.9. $C_{19}H_{18}O_3$ requires C, 77.6 ; H, 6.2%).

Claisen Condensation of Orcacetophenone Dimethyl Ether with Ethyl Phenylacetate : Sodium Salt of β-Diketone, 2 : 4-Dimethoxymethylbenzoylphenylacetyl-methane.—A solution of orcacetophenone dimethyl ether (6 g., 1 *M*) and ethyl phenylacetate (17 g., 4 *M*) in dry xylene was gradually added to the flask containing pulverised sodium (1.5 g, 2 *M*), the container being cooled externally by cold water. After the initial reaction had subsided, the reaction mixture was heated in an oil-bath at 120° for 2 hours. On cooling, the sodium salt formed was filtered, washed with dry ether several times and was finally dried.

1-(2:4-Dimethoxy-6-methylbenzoyl)-1-phenylacetyl-ethane.—The above dry sodium salt (4 g.) was suspended in dry acetone and methyl iodide (1.5 c.c.) was added to it. The resulting mixture was refluxed on a steam-bath for 5 hours. Most of the acetone was distilled off and the reaction mixture was diluted with water, when a dark oil separated out. This was extracted with ether, washed with water and dried. The removal of the ether gave an oil which could not be purified further and, hence, it was subjected to cyclisation as described below.

7-Methoxy-2-benzyl-3:5-dimethylchromone.—The above crude β-diketone (0.5 g.) was warmed with hydrobromic acid in acetic acid (35%, 2 c.c.) for half an hour and left overnight at room temperature. Next day, on pouring the reaction mixture in ice-water a brown pasty mass separated out. It was crystallised from alcohol (charcoal) in white stout needles, m.p. 125-26°, yield 0.2 g. It is insoluble in alkali and does not exhibit any coloration with ferric chloride.

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SUBSTITUTED DICARBOXYLIC ACIDS. PART II. SYNTHESIS OF DICHLOROPHENYL- AND METHOXYNAPHTHYL-SUCCINIC ACIDS

By K. J. Shah, D. K. Genge and J. J. Trivedi

Using Lapworth's method 2:4- and 2:5-dichlorophenyl-, 2-methoxy-1-naphthyl- and 4-methoxy-1-naphthyl-succinic acids have been synthesised.

The purpose of synthesising substituted dicarboxylic acids as well as the synthesis of some substituted succinic acids were reported in Part I of the series (Genge and Trivedi, this *Journal*, 1957, **34**, 915). In this communication we report the synthesis of dichlorophenyl- and substituted naphthyl-succinic acids using 2:4- and 2:5-dichlorobenzaldehydes and 2- and 4-methoxy-1-naphthaldehydes. Dicyano compound from methoxynaphthaldehydes has been satisfactorily converted into the substituted succinic acid by acid hydrolysis, followed by an alkaline hydrolysis.

Experimental

2:5-Dichlorobenzaldehyde was prepared by Beech's method as described by Nargund *et al.* (*J. Karnatak Univ.*, 1956, **1**, 61). 2:4-Dichlorobenzaldehyde was of Eastman's practical grade. 2-Hydroxy-1-naphthaldehyde was prepared in 82% yield from β-naphthol by the Reimer-Tiemann method (Fosse, *Bull. soc. chim.*, 1901, *iii*, **25**, 373), while 4-hydroxy-1-naphthaldehyde was prepared in 55% yield from α-naphthol according to the method of Adams and Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2375). These were methylated by dimethyl sulphate and caustic soda.

Preparation of sodium cyanoacetate, its condensation with aldehydes and preparation of the dicyano compounds and their hydrolysis to succinic acids were carried out as described previously (Genge and Trivedi, *loc. cit.*). In the case of dicyano compound in the naphthalene series, the following method was followed.

Hydrolysis of the Dicyano Compound in the Naphthalene series.—A mixture of dicyano compound [prepared from 35 g. of ethyl-α-cyano-β-(2/4-methoxy-1-naphthyl)-acrylate], HCl (conc., 150 c.c.) and water (20 c.c.) was refluxed on a sand-bath for 6 hours. After decanting off the aqueous solution, the residue was refluxed with 10% aqueous KOH (150 c.c.) for 6 hours. The alkaline filtrate on acidification afforded the substituted succinic acid. To obtain a colorless product, the substance was purified through its anhydride. The succinic acids and their derivatives are shown in Table IA and Table IB. All m.p.s are uncorrected.

TABLE Ia

S. No.	Compounds.	M.P.	Cryst. shape.	Formula.	% Chlorine. Found.	Calc.
*1	α-Cyano-β-2:4-dichlorophenylacryiic acid	189°	Needles from EtOH	$C_{10}H_5O_2NCl_2$	29.5 (246.5)	29.4 (242.0)
2	Ethyl ester of (1)	72°	Do	$C_{12}H_9O_2NCl_2$	26.1	26.3
3	2:4 Dichlorophenylsuccinic acid	175°	Granules from hot water	$C_{10}H_8O_4Cl_2$	27 0 (134.0)	27.1 (131.5)
4	Mono-*p*-toluidide of (3)	154°	Needles from EtOH	$C_{17}H_{15}O_3NCl_2$	20.3 (348.0)	20.2 (352.0)
5	Dianilide of (3)	138°	Do	$C_{22}H_{18}O_2N_2Cl_2$	17.3	17.2
6	Di-*p*-toluidide of (3)	158°	Do	$C_{24}H_{22}O_2N_2Cl_2$	15.9	16.1
7	Imide of (3)	80°	Needles from dil. EtOH	$C_{10}H_7O_2NCl_2$	29 3	29.1
8	Anhydride of (3)	154°	Needles from benzene-petrol	$C_{10}H_6O_3Cl_2$	28.8	29.0
9	α-Cyano-β-2:5-dichlorophenylacrylic acid	176°	Needles from dil. EtOH	$C_{10}H_5O_2NCl_2$	29.5 (246.5)	29.4 (242.0)
10	Methyl ester of (9)	112°	Needles from EtOH	$C_{11}H_7O_2NCl_2$	27.8	27.9
11	2:5-Dichlorophenylsuccinic acid	226°	Granules from hot water	$C_{10}H_8O_4Cl_2$	27.0 (134.0)	27.1 (131.5)
12	Mono-*p*-toluidide of (11)	188°	Needles from EtOH	$C_{17}H_{15}O_3NCl_2$	20.1 (350.0)	20.2 (352.0)
13	Dianilide of (11)	110° (decomp.)	Needles from benzene-petrol	$C_{22}H_{18}O_2N_2Cl_2$	17.3	17.2
14	Di-*p*-toluidide of (11)	135°	Granules from dil. EtOH	$C_{24}H_{22}O_2N_2Cl_2$	15.9	16.1
15	Imide of (11)	175°	Granules from hot water	$C_{10}H_7O_2NCl_2$	29.3	29.1
16	Anhydride of (11)	107°	Needles from benzene-petrol	$C_{10}H_6O_3Cl_2$	28.8	29.0

* Chem. Abs , 1956, **50**, 15577 ; Ethyl. Corp. Pat. 737, 753/1955 report m.p. 189°-191°.

TABLE Ib

S. No.	Compounds.	M.P.	Cryst. shape.	Formula.	Analysis. Found.	Calc.
17	α-Cyano-β-(2-methoxy-1-naphthyl)-acrylic acid	225°	Yellow plates from acetic acid	$C_{15}H_{11}O_3N$	C, 70.9 H, 4.1 (250.3)	71.2 4.3 (253.0)
18	Ethyl ester of (17)	85°	Yellow plates from EtOH	$C_{17}H_{15}O_3N$	C, 72.4 H, 5.0	72.6 5.3
19	Methyl ester of (17)	119°	Shining yellow needles from EtOH	$C_{16}H_{13}O_3N$	C, 71.6 H, 4.6	71.9 4.9
20	2-Methoxy-1-naphthylsuccinic acid	185°	Shining prisms from acetic acid	$C_{15}H_{14}O_5$	C, 65.3 H, 4.8 (136.1)	65.7 5.1 (137.0)
21	Monoanilide of (20)	167°	Colorless plates from dil. EtOH	$C_{21}H_{19}O_4N$	(347.0)	(349.0)
22	Mono-*p*-toluidide of (20)	212°	Colorless needles from dil. EtOH	$C_{22}H_{21}O_4N$	(360.6)	(363.0)
23	Imide of (20)	215°	Granules from EtOH	$C_{15}H_{13}O_3N$	N, 5.3	5.5
24	Anhydride of (20)	149°	Granules from acetic acid	$C_{15}H_{12}O_4$	C, 70.2 H, 4.5	70 3 4.7
25	α-Cyano-β-(4-methoxy-1-naph.hyl)-acrylic acid	230°	Yellow plates from acetic acid	$C_{15}H_{11}O_3N$	C, 70.8 H, 4.1 (252.2)	71.2 4 3 (253.0)

TABLE Ib (contd.)

S. No	Compounds.	M.P.	Cryst. shape.	Formula.	Analysis. Found.	Calc.
26	Ethyl ester of (25)	86°	Yellow plates from EtOH	$C_{17}H_{15}O_3N$	C, 72.3 H, 5.1	72.6 5.3
27	Methyl ester of (25)	121°	Yellow needles from EtOH	$C_{16}H_{13}O_3N$	C, 71 8 H, 4.5	71.9 4.9
28	4-Methoxy-1-naphthyl-succinic acid	224°	Granules from acetic acid	$C_{15}H_{14}O_5$	C, 65.4 H, 4.8 (135 0)	65.7 5.1 (137.0)
29	Monoanilide of (28)	180°	Plates from dil. EtOH	$C_{21}H_{19}O_4N$	(347.8)	(349.0)
30	Mono-*p*-toluidide of (28)	182°	Needles from dil. EtOH	$C_{22}H_{21}O_4N$	(362.7)	(363.0)
31	Imide of (28)	203°	Granules from EtOH	$C_{15}H_{13}O_3N$	N, 5.2	5.5
32	Anhydride of (28)	106°	Needles from petrol	$C_{15}H_{12}O_4$	C, 70.0 H, 4.3	70.3 4.7

N.B. The figures within parantheses in last two columns refer to equivalents.

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USE OF DIPHENYLTHIOVIOLURIC ACID AS A REAGENT FOR GRAVIMETRIC ESTIMATION OF METALS. PART II. ESTIMATION OF IRON

By R. P. Singh

Diphenylthiovioluric acid has been found to be a suitable reagent for the gravimetric estimation of iron. The metal can be estimated both in ferrous and ferric conditions by this reagent. The compounds precipitated in the two cases are different. *p*H control is absolutely necessary to obtain quantitative results in the case of both ferrous and ferric iron.

It was observed previously that diphenylthiovioluric acid formed numerous complex salts with metals (Gambhir and Singh, *Proc. Ind. Acad. Sci.*, 1946, **23A**, 330). It was found that the complexes with ferrous and ferric iron were dark blue and dark green respectively. Subsequently, it was found that the ammonium salt of diphenylthiovioluric acid could be used as a suitable reagent for the gravimetric estimation of copper (Singh and Shankar, this *Journal*, 1955, **32**, 557). This work has now been extended to the estimation of iron by this reagent and conditions for obtaining quantitative precipitates have been worked out in the case of iron in both the valency states.

Experimental

Ammonium salt of diphenylthiovioluric acid was prepared by the method described by Singh and Shankar (*loc. cit.*). A 0.8% solution of the ammonium salt was used in all estimations.

Estimation of Fe^{II}.—Ferrous ammonium sulphate (A.R., B D.H.) was used for preparing standard solutions of iron. The purity of the sample, as determined by volumetric and gravimetric methods, was found to be 99.8%. The ferrous salt (10 c.c.) containing about 0.03 g. of iron was taken for each estimation. Boiled distilled water was used throughout for preparing the solutions to avoid oxidation of iron. Atmospheric oxidation of ferrous iron was further prevented by adding 2 c.c. of 0.2% hydroquinone solution for every 10 c.c. of iron solution. Absence of ferric iron was confirmed in the solution by testing with potassium ferrocyanide before estimation.

Estimation of iron in nearly neutral solutions, without adjusting the *p*H, showed that precipitation was not quantitative. The effect of change of *p*H was then studied with a view to ascertaining conditions for the quantitative precipitations.

It has been found that the results are fairly accurate when precipitations are carried out between the *p*H range of 4.9–5.6. Below *p*H 4.5, diphenylthiovioluric acid was found to precipitate. *p*H measurements were carried out by means of a Beckman *p*H meter. It was also found that a sufficient excess of the reagent (thrice the theoretical amount for ferrous and twice for ferric) should be added for complete precipitation. In the estimations described below, still larger quantities were added to avoid errors due to incomplete precipitation. The following procedure was adopted for these estimations.

A freshly prepared solution (10 c.c.) of ferrous ammonium sulphate containing about 0.03 g. of iron and a small quantity of hydroquinone (2 c.c. of 0.2% soln.) was diluted to 40 c.c. A requisite quantity of dilute sulphuric acid or ammonia was added till the *p*H of the solution was between 4.9 and 5.6. The solution was heated on a water-bath and to the hot solution the reagent solution was gradually added with constant stirring till complete precipitation and the filtrate did not respond to a test for iron. The precipitate was digested on a water-bath for about an hour and left overnight. It was then filtered through a sintered glass crucible No. 4 under gentle suction. The precipitate was washed thoroughly with hot distilled water till free of SO_4^{2-} and finally dried in a constant-temperature oven at 115°. The results of estimations are shown in Table I.

TABLE I

Vol. of Fe^{II} soln. for each estimation = 10 c.c.
Conc. of the ammonium salt soln. = 0.8%.
Ammonium salt soln. added each time = 240 c.c.

No.	*p*H.	Wt of iron in soln. Found.	Calc.	% Error.
1	4.9	0.02300 g.	0.02898 g.	0 07
2	5.0	0.03590	0.03575	0.43
3	5.2	0.02676	0.02670	0.23
4	5.4	0.02670	0.02672	0 07
5	5.5	0.02665	0.02670	0.20
6	5.6	0.03563	0.03575	0.34

Estimation of Fe^{III}.—Estimations of iron in the ferric state were carried out on similar lines. The procedure for precipitation was identical with that used for ferrous iron except that no hydroquinone was added and *p*H had to be adjusted between 4.9 and 5.8. The results of estimations under these conditions are recorded in Table II.

TABLE II

Vol. of Fe^{III} soln. for each estimation = 10 c.c.
Conc. of the ammonium salt soln. = 0.8%.
Ammonium salt soln. added each time = 250 c.c.

No.	*p*H.	Wt. of iron in soln. Found.	Calc.	% Error,
1	4.9	0.02476 g.	0.02472 g.	0.16
2	5.1	0.02475	0.02472	0.125
3	5.3	0.02450	0.02460	0.40
4	5.5	0.02477	0.02472	0.21
5	5.7	0.02476	0.02466	0.40
6	5.8	0.02470	0.02466	0.16

Estimations of ferrous and ferric iron can thus be carried out fairly accurately under the above conditions.

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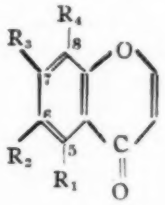
NITRATION OF CHROMONES

By P. P. Joshi, T. R. Ingle and B. V. Bhide

The nitration of chromones, substituted in the benzene ring only, has been studied. Position-8 has been found to be the active position in 5- and 7-substituted chromones; while position-5 appears to be more reactive in the case of 6-substituted chromones In the case of chromone, however, position-6 shows marked reactivity.

Nitration of chromones does not appear to have been studied so far in detail. Shah *et al.* (*Proc. Ind. Acad. Sci.*, 1949, **29A**, 315; 1953, **38A**, 31) nitrated 7-hydroxy- and 5-hydroxy-chromone derivatives, while Desai *et al.* (*J. Sci. Ind. Res.*, 1954, **13B**, 328; this *Journal*, 1954, **31**, 145) nitrated and brominated 7-hydroxy- and 5-hydroxy-chromone derivatives, and to them position-8 appeared to be reactive in those derivatives, supporting Mills-Nixon effect (*J. Chem. Soc.*, 1930, 2510).



The present work describes the nitration of chromones, substituted in the benzene ring only. The chromones required for the present work were prepared by the method of Späth and Lederer (*Ber.*, 1930, **63**, 743), slightly modified so that the yields of chromones were of the order of 50%. Nitration of chromones was carried out at 0° by the nitrating mixture (H_2SO_4, *d* 1.8, 3 parts; HNO_3, *d* 1.42, 1 part). In all the chromones, mononitro product was obtained in almost quantitative yield. The position of the nitro group has been determined in each chromone either (1) by identifying the product obtained after alkaline hydrolysis, or (2) by identifying chromone, or (3) by synthesising the nitrochromone by an unambiguous method. The results obtained are tabulated below.

TABLE I

	Chromones used.	Nitrochromones obtained.
1.	5-Methoxy-	5-Methoxy-8-nitro-
2.	7-Methoxy-	7-Methoxy-8-nitro-
3.	7-Hydroxy-	7-Hydroxy-8-nitro-
4.	6-Methoxy-	6-Methoxy-5-nitro-
5.	6-Hydroxy-	6-Hydroxy-5-nitro-
6.	6-Chloro-	6-Chloro-5-nitro-
7.	Chromone.	6-Nitrochromone

The above observations indicate that, in the case of substitution at positions 5 and 7, the nitro group enters the position-8, while in the case of chromones having substituents at '6', the nitro group enters the position-5. In the case of simple chromone, however, the position-6 appears to be markedly reactive.

EXPERIMENTAL

5-Methoxychromone (R_1 = OMe; R_2 = R_3 = R_4 = H).—A well-cooled solution of 6-methoxy-2-hydroxyacetophenone, prepared by the method of Gangal and Limaye (*Rasayanam*, 1936, **1**, 31) (16.6 g., 0.1 *M*) in freshly distilled ethyl formate (25 c.c.) and dry ether (50 c.c.), was added in small lots with stirring to powdered sodium (7 g., 0.3 *M*), suspended in dry ether (50 c.c.). The reaction mixture was kept for 4 hours in ice and then overnight at room temperature. Ethyl formate-ether mixture (1 : 10) was added and the total reaction mixture was refluxed for 1 hour. On cooling, water (100 c.c.) was added to it carefully and the alkaline layer was separated. The alkaline layer was acidified by 50% H_2SO_4 till it was strongly acidic (above 30% w.r.t. H_2SO_4) and heated on a water-bath for 1 hour. It was cooled and neutralised with solid sodium bicarbonate when the chromone separated as a solid. It was filtered, washed with dilute alkali and finally with water till free from alkali. The chromone is soluble in ethyl and methyl alcohols, acetone, ethyl acetate, benzene and ether. It is sparingly soluble in water, petroleum ether. It was crystallised from petroleum ether (b.p. 60-80°), m.p. 83-84°. (Found : C, 68.4 ; H, 4.5. $C_{10}H_8O_3$ requires C, 68.19 ; H, 4.54%).

5-Methoxy-8-nitrochromone (R_1=OMe ; R_2=R_3=H ; R_4=NO_2).—5-Methoxychromone (1 g.), dissolved in H_2SO_4 (*d* 1.8, 5 c.c.), was nitrated by the nitrating mixture (H_2SO_4 *d* 1.8, 1.2 c.c. and HNO_3 *d* 1.42, 0.4 c.c.) at 0°. The reaction mixture was maintained at 0° for 4 hours and was poured over crushed ice. The nitrochromone separated as a yellow solid. It is soluble in ethyl and methyl alcohol, acetone, benzene, sparingly soluble in water and petroleum ether. It was crystallised from benzene in needles, m.p. 201-203°. (Found : N, 6.5. $C_{10}H_7O_5N$ requires N, 6.3%).

Hydrolysis of 5-Methoxy-8-nitrochromone: Isolation of 3-Nitro-2 : 6-dihydroxyacetophenone.—5-Methoxy-8-nitrochromone (1 g.) was suspended in NaOH solution (25 c.c., 1*N*) and refluxed for 1 hour when it became a clear solution. It was cooled, acidified to Congo red and the solid separating was collected, washed with water and dried. It was crystallised from dilute alcohol in fine needles, m.p. 118-19°. (Found : N, 7.3. Calc. for $C_8H_7O_5N$: N, 7.1%). It did not depress the m.p. of 3-nitro-2 : 6-dihydroxyacetophenone, prepared by the method of Naik and Shah (*Proc. Ind. Acad. Sci.*, 1953, **37A**, 785). This observation indicates that during hydrolysis demethylation has taken place. As both 5-methoxy-6-nitro- and 5-methoxy-8-nitrochromone can yield on demethylation the above product, this result does not lead to any definite conclusion.

8-Nitro-5-methoxychromone was also prepared according to the procedure described under 5-methoxychromone, using 3-nitro-2-hydroxy-6-methoxyacetophenone as the starting material. It was crystallised from benzene, m.p. 202-203°.

The mixed m.p. of this chromone and the one obtained by the nitration of 5-methoxychromone remained unchanged.

The nitrations of other chromones have been studied in a similar manner. The chromones were synthesised by the procedure adopted for 5-methoxychromone and nitrations carried out as described under 8-nitro-5-methoxychromone. Conditions used for alkaline hydrolysis were the same as described under the hydrolysis of 8-nitro-5-methoxychromone.

The following procedures were adopted for the oxidation of nitrochromones and methylation of hydroxychromones.

Oxidation of Nitrochromone by $KMnO_4$.—To the chromone (1 g.), dissolved in acetone (10 c.c.), powdered $KMnO_4$ (8 g.) was added in small lots. The mixture was refluxed for 1 hour for complete oxidation. It was then cooled, diluted with hot water and filtered. The residue was also washed with hot water (3 × 25 c.c.). The filtrate and washings (about 100 to 150 c.c.) were concentrated to a small volume (5 c.c.) and acidified with HCl (dil.) to Congo red, when a solid separated. It was filtered, washed, dried and generally crystallised from dilute alcohol.

Methylation of Hydroxychromone by MeI *and* K_2CO_3.—To the hydroxychromone (1 g.), dissolved in dry acetone (20 c.c.), anhydrous potassium carbonate was added, followed by methyl iodide (5 c.c.) in small lots. The reaction mixture was afterwards refluxed for 24 hours and filtered hot. The residue was extracted with dry acetone. On removal of acetone, a solid separated. It was washed with water, filtered, dried and crystallised from alcohol.

Compounds obtained during the nitrations of different chromones are summarised in Table. II. References for the methods of preparing the starting materials required for chromones are noted against them in Table II.

TABLE II

S. N.	Compound. (C = chromone).	Material and method.	M.P.	Formula.	% Nitrogen. Found.	Calc.	Cryst. from.
			7-Methoxychromone.				
(i)	7-Methoxy-C	2-Hydroxy-4-methoxy-acetophenone (Crabtree & Robinson, *J. Chem. Soc.*, 1918, **113**, 868).	110° (Kostanecki *et al.*, *Ber.*, 1902, **35**, 865, report m.p. 110°).		...	...	Pet. ether (60-80°)
(ii)	7-Methoxy-8-nitro-C	Nitration of (i)	226°	$C_{10}H_7O_5N$	6.5	6.33	Ethyl acetate
(iii)	2-Hydroxy-4-methoxy-3-nitro-aceto-phenone	Alkali hydro-lysis of (ii)	204-205°	$C_9H_9O_5N$	6.9	6.63	Benzene
(iv)	Semicarbazone of (iii)		>300°	$C_{10}H_{12}O_5N_4$	1.97	2.08	EtOH
(v)	2:4-Dimethoxy-3-nitro-acetophe-none	Methylation of (iv).	54-55°	$C_{10}H_{11}O_5N$	6.4	6.22	EtOH
(vi)	Semicarbazone of (v)		228-30°	$C_{11}H_{14}O_5N_4$	1.9	1.98	EtOH
(vii)	2:4-Dimethoxy-3-nitrobenzoic acid	Oxidation of (v) by $KMnO_4$.	210-12°	$C_9H_9O_6N$	6.3	6.12	Water
				Equiv.	227.5	227.0	

TABLE II (contd.)

S. N.	Compound. (C=chromone).	Material and method.	M.P.	Formula.	% Nitrogen. Found.	Calc.	Cryst. from.
	Authentic sample of (vii)	Prepared by the method of Dadswell and Kenner (*J. Chem. Soc.*, 1927, 587)	210-11° Mixed m.p. of (vii) and authentic sample, 210°.	...			...
			7-Hydroxychromone.				
(i)	7-Hydroxy-C	Demethylation of 7-methoxy-C.	218° (Kostanecki *et al.*, *loc. cit.*)				
(ii)	7-Hydroxy-8-nitro-C	Nitration of (i).	268-70°	$C_9H_5O_5N$	6.9	6.76	EtOH
(iii)	7-Methoxy-8-nitro-C	Methylation of (ii) by K_2CO_3 and MeI.	226°	$C_{10}H_7O_5N$	6.5	6.33	Ethyl acetate
(iv)	2 :4-Dihydroxy-3-nitro-acetophenone	Hydrolysis of (ii).	95-96°	$C_8H_7O_5N$	7.3	7.10	Benzene
(v)	Semicarbazone of (iv)	...	210-12°	$C_9H_{10}O_5N_4$	2.15	2.20	EtOH.
			6-Methoxychromone.				
(i)	6-Methoxy-C	2-Hydroxy-5-methoxyacetophenone (Kostanecki and Lampe, *Ber.*, 1904, **37**, 774).	97-98° (Ingle *et al.*, this *Journal*, 1949, **26**, 569, report m.p. 97°).	...	...	...	Pet. ether (60-80°)
(ii)	6-Methoxy-5-nitro-C	Nitration of (i).	216-17°	$C_{10}H_7O_5N$	6.5	6 3	EtOH
(iii)	5-Methyl ether of 6-nitrogentisic acid	Oxidation of (ii) by $KMnO_4$.	220-21° (Klemenc, *Monatsh.*, 1914, **35**, 103, report m.p. 220-21°).	$C_8H_7O_6N$	7.0 Equiv. 213	6.8 212.6	Water
(iv)	2-Hydroxy-5-methoxy-6 nitro-acetophenone	Hydrolysis of (ii)	158-60°	$C_9H_9O_5N$	6.9	6.6	Benzene
(v)	Semicarbazone of (iv)		210-12°	$C_{10}H_{12}O_5N_4$	1.9	2.0	EtOH
			6-Hydroxychromone.				
(i)	6-Hydroxy-C	2-Acetylhydroquinone.	241-42° (David & Kostanecki, *Ber.*, 1902, **35**, 2547, reportm.p 243°).	...	...	...	MeOH
(ii)	5-Nitro-6-hydroxy-C	Nitration of (i).	260-62°	$C_9H_5O_5N$	6.9	6.76	EtOH
(iii)	5-Nitro-6-methoxy-C	Methylation of (ii) by K_2CO_3 and MeI.	217° (mixed m p.)	$C_{10}H_7O_5N$	6.4	6.33	EtOH

TABLE II (contd.)

S. N.	Compound. (C=chromone).	Material and method.	M.P.	Formula.	% Nitrogen. Found.	Calc.	Crvst. from.
			6-Chlorochromone.				
(i)	6-Chloro-C	5-Chloro-2-hydroxyacetophenone (Auwers & Wittig, *Ber.*, 1924, **57**, 1270).	140-42°	$C_9H_5O_2Cl$	C:60.2 H: 3.1	60.0 2.8	Dil. EtOH
(ii)	6-Chloro-5-nitro-C	Nitration of (i).	180-82°	$C_9H_4O_4NCl$	6.4	6.2	Do
(iii)	5 Chloro 6-nitrosalicyclic acid	Oxidation of (ii) by $KMnO_4$.	215-17°	$C_7H_4O_5NCl$	6.8 Equiv. 217	6.5 217 5	Water
(iv)	4-Chloro-3-nitrophenol	Decarboxylation of (iii) by heating its Ca salt under reduced pressure at 290-300°.	125-26° (Van Erp, *J. prakt. Chem.*, 1930, **127**, 31, reports m.p. 126-27°)	$C_6H_4O_3NCl$	7.8	8.0	Do
			Chromone.				
(i)	Chromone	*o*-Hydroxyacetophenone (Org. Syn. **13**, p. 92).	59° (Ruhemann & Stepelton, *J. Chem. Soc.*, 1900, **73**, 1179 report m.p. 59).	...	...	...	Pet. ether (60-80°)
(ii)	6-Nitro-C	Nitration of (i).	170-71°	$C_9H_5O_4N$	7.5	7.3	EtOH
(iii)	3-Nitro-6-hydroxyacetophenone	Hydrolysis of (ii).	99°	$C_8H_7O_4N$	7.9	7.7	Benzene
	Authentic sample	Prepared by the method of Joshi & Harisinγh (*J. Amer. Chem. Soc.*, 1954, **76**, 4993).	99° (mixed m.p.)	...	...	...	

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SHORT NOTES

CYANINE DYES FROM 4-METHYLCINNOLINE

By A. B. Lal

Cyanine dyes from heterocyclic compounds containing one nitrogen atom in the ring, such as, quinaldine, lepidine, 2-picoline, etc., are well known. Besides these, dyes from benzthiazole and benzoxazole ring systems have also proved of great value. It, however, appears that little attention has been paid to the preparation of dyes from heterocyclic ring systems containing more than one nitrogen atom. The first successful attempt in this direction was that of Heilbron and coworkers (*J. Chem. Soc.*, 1932, 251) who prepared dyes from 4-substituted quinazoline. Cyanine dyes have also been prepared from quinoxaline (Cook *et al.*, *ibid.*, 1942, 710). Recently Mann *et al.* also made an attempt in this direction (*ibid.*, 1956, 1331), but reported failure.

As a part of a comprehensive programme of investigations in the field of cyanine dyes, preparation of dyes from heterocyclic systems having two nitrogen atoms in one ring has been undertaken. The present communication describes some of the cyanine dyes prepared from 4-methylcinnoline (Lal, this *Journal*, 1957, **34**, 425).

4-*Methylcinnoline methiodide* was obtained by boiling the base and methyl iodide in alcohol, m.p. 206°. (Found : N, 10.15; I, 43.82. $C_{10}H_{11}N_2I$ requires N, 9.79 ; I, 44.32%).

4-p-*Dimethylaminostyrylcinnoline methiodide* was obtained by adding a mixture of the quaternary salt and *p*-dimethylaminobenzaldehyde to warm acetic anhydride and triethylamine, m.p. 251°. (Found : N, 10.31 ; I, 30.2. $C_{19}H_{20}N_3I$ requires N, 10.07 ; I, 30.69%). The corresponding ethiodide was prepared similarly, but gave low values of N and I on analysis.

bis-[4-(1-*Ethylcinnoline*)]-*trimethinecyanine iodide* was prepared by refluxing 4-methylcinnoline ethiodide in a mixture of acetic anhydride and ethyl orthoformate, m.p. 253.5°. (Found : N, 11.30 ; I, 25.97. $C_{23}H_{23}N_4I$ requires N, 11.61 ; I, 26.34%).

[4-(1-*Methylcinnoline*)] [4-(1-*methylquinoline*)]-*trimethinecyanine iodide* was prepared by adding a mixture of 4-anilinovinylcinnoline methiodide (m.p. 236°) and lepidine methiodide to acetic anhydride containing triethylamine, m.p. 250.5°. (Found : N, 9.12 ; I, 28.46. $C_{22}H_{20}N_3I$ requires N, 9.27 ; I, 28.03%).

[4-(1-*Ethylcinnoline*)] [2-(1-*ethylquinoline*)]-*trimethinecyanine iodide* was prepared as above from 4-anilinovinylcinnoline ethiodide (m.p. 228°) and quinaldine ethiodide, m.p. 263°. (Found : N, 8.97 ; I, 26.22. $C_{24}H_{24}N_3I$ requires N, 8.73 ; I, 26.40%).

Further work is in progress and the photographic sensitising properties of these dyes are under investigation.

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PRACTICAL PROTON-LIGAND STABILITY CONSTANTS OF SOME NITROCATECHOLS

By K. S. Math, K. A. Venkatachalam and M. B. Kabadi

In a study of the influence of nuclear substituents on the solution stability constants of metal-catechol complexes, it became necessary to determine the dissociation constants of some nitrocatechols. These have been obtained as the practical proton-ligand stability constants (Irving and Rossotti. *J. Chem. Soc.*, 1954, 2904) in aqueous medium at 30° and $\mu \sim 0.1M$, by the Calvin-Bjerrum-*p*H titration technique as modified by Irving and Rossotti (*loc. cit.*). The concentrations of the various quantities were: $T_L°$ (reagent) $\approx$ $0.004M$, $E°$ (free $HClO_4$) $\approx 0.02M$, N (normality of alkali) ≈ 1 and $[NaClO_4] \approx 0.1M$. The values of the constants are recorded in Table I.

TABLE I

Compounds.	Method of solution of formation function.	Log $^pK_1^H$. Found.	Calc.	Log $^pK_2^H$. Found.	Calc.
Catechol	Least square	11.74	...	9.28	9.28
3-Nitrocatechol	Average*	11.48	10.24	6.50	6.28
4-Nitrocatechol	Least square	10.59	10.24	6.63	6.28
3:4-Dinitrocatechol	Half integral	8.24	7.24	4.02	4.78
3:5-Dinitrocatechol	Average*	9.86	8.74	3.32	3.28

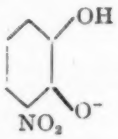
*Average of log $^pK^H$ values obtained by treating the two steps of the formation curve as for monobasic acids.

The difference log $^pK_1^H$ − log $^pK_2^H$ is of the order of 4 or greater in all cases except catechol so that the two OH groups of these compounds can be regarded as dissociating stepwise. An examination of the molecular structures of these compounds shows that 2-OH will dissociate first in the case of 3-nitro and 3:5-dinitro compounds and 1-OH in the case of the 4-nitro, owing to favourable inductive and mesomeric effects of the NO_2 groups. In the case of the 3:4-dinitro compound, the relative position of both the OH groups with respect to the NO_2 groups, regarding the mesomeric effect, is same. However, as the inductive effect diminishes with distance, the proximity of the NO_2 groups to the 2-OH indicates that it dissociates first here too. It is, of course, impossible to distinguish between the two OH groups in the case of catechol.

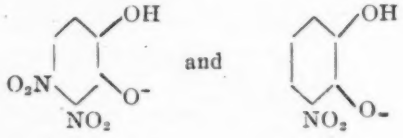
A semi-quantitative estimate of the inductive and mesomeric effects of the NO_2 groups can be had by following Pauling ("The Nature of the Chemical Bond", Ithaca, New York, Cornell University Press, 2nd ed., 1945, pp. 205-6), according to whom, 'the acid constant of a nitrophenol can be found approximately by multiplying that for phenol itself by the factor 32 for every *meta*-nitro group and 1000 for every *ortho* or *para*-nitro group in the molecule'. Using the practical constants for catechol, the $^pK^H$ values of the nitro derivatives have been calculated accordingly and shown in Table I. It is seen that there is a fair agreement for all log $^pK_1^H$ values

except in the case of 3 : 4-dinitro, and no agreement for any log $^{p}K_1^{II}$ value except for 4-nitro. The low (exp.) log $^{p}K_1^{II}$ value of the 3 : 4-dinitro compound may be due to withdrawal of electrons from the 3-nitro group by the 4-NO_2 and consequent withdrawal of a greater number of electrons from the 2-OH by 3-NO_2. Such a possibility is indicated when the pK values of 2 : 3-dinitrophenol (4.92) and *o*-nitrophenol (7.12) (Pauling, *loc. cit.*) are compared. If the 3-NO_2 were exerting on the OH, only the effect expected from its *meta* position with respect to the latter, the pK value should have been 5.62, which is 0.7 unit higher than the experimental value. The withdrawal may take place by the electron-attracting inductive effect only so that it can be exhibited even if the two NO_2 groups are not in the same plane.

The difference between the log $^{p}K_1^{II}$ values of catechol and the 3-nitro derivative is not very great while the calculated value for the latter differs from the experimental by more than 1.0 unit. This indicates a partial quenching of the influence of the *meta*-nitro group (the inductive effect) on the 1-OH. The quenching might be due to the negative charge on the 2-O, since the structure of the corresponding unionised acid is



The negative charge can satisfy the electron-attracting inductive effect of the 3-NO_2. This view is substantiated by considering the differences, log $^{p}K_1^{II}$ (catechol) — log $^{p}K_1^{II}$ (3:4-dinitrocatechol) and log $^{p}K_1^{II}$ (catechol) — log $^{p}K_1^{II}$ (3 : 5-dinitrocatechol). The values are 3.50 and 1.88 respectively and are much lower than 4.50 and 3.00 respectively, which are expected if the *meta* effect (inductive effect) of the 3-NO_2 were not quenched in the 3 : 4 and 3 : 5 compounds in which cases also the structures of the relevant unionised acids respectively are :



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REFRACTOMETRIC DETERMINATION OF TRANSITION POINTS

By M. A. Azim and Mazhar-Ul-Haq

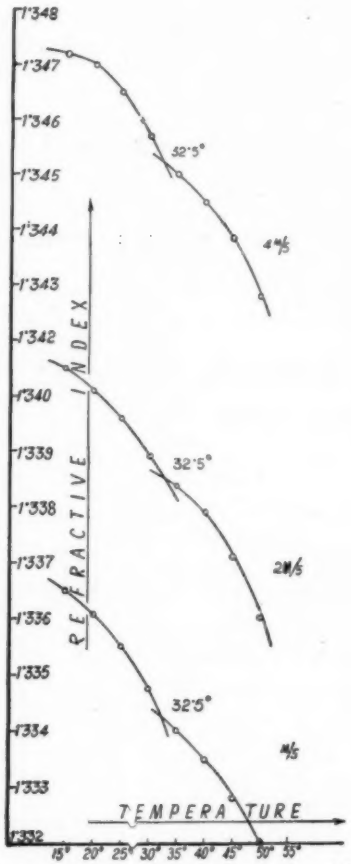

FIG. 1

Transition points of hydrates are determined usually by taking advantage of sudden variations in certain physical properties of the hydrates at transition temperatures. Refractive index, being a physical property, which could be easily and accurately measured, should also provide a means for such determinations, as demonstrated by the work of Joshi and Joshi (this *Journal*, 1956, **33**, 149). This method has been employed in the present work for the study of four hydrates, by following the variation in the indices of 0.8*M* solutions with variation in temperature between 15° and 60°. The results are shown in Fig. 1. Abrupt changes at the transition points are quite marked. The transition temperatures found by this method are very nearly the same as the ones recorded in standard literature.

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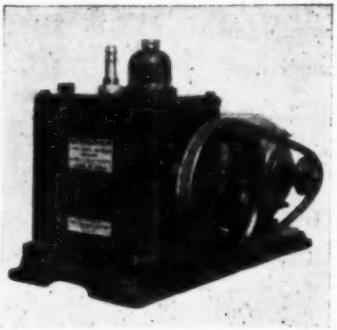

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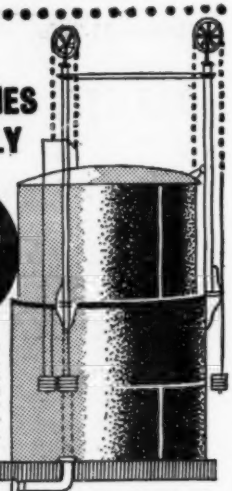

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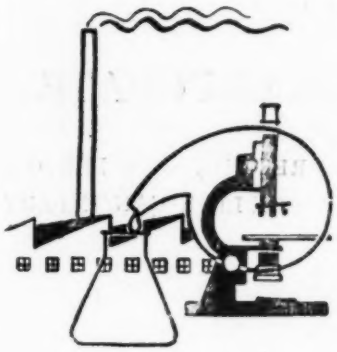

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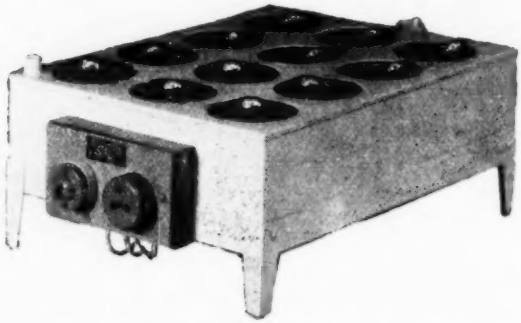

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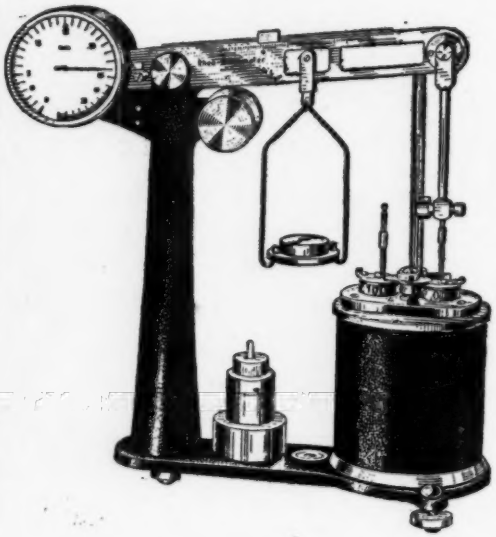

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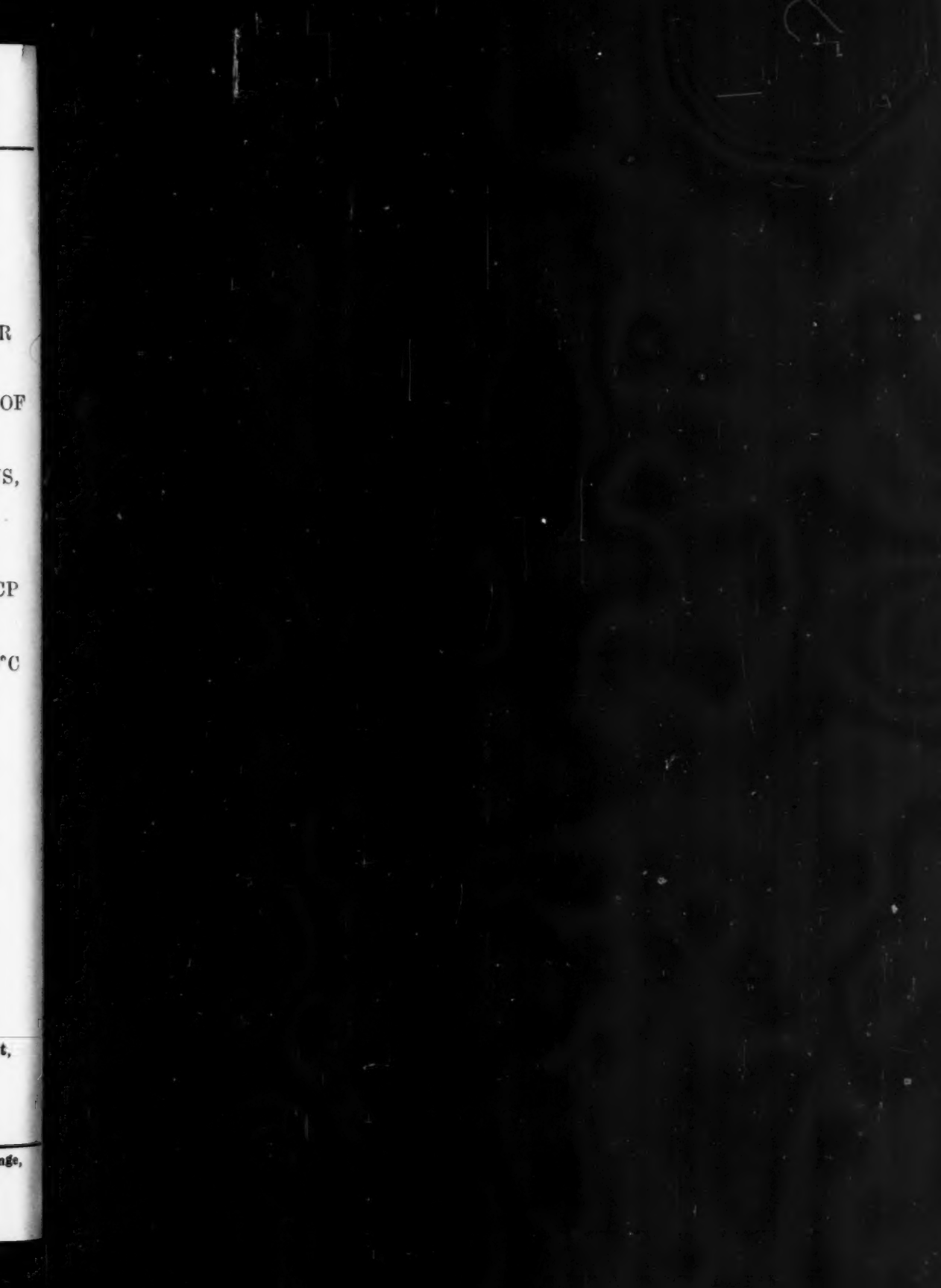
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